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**Proceedings Paper:**

Gallelo, Gianni, Ramacciotti, Mirco, Lezzerini, Marco et al. (5 more authors) (2017) The source of the building stones from the Sagunto Castle archaeological area and its surroundings. In: Corozzi, Alessandro, (ed.) Abstract Book CSI XL PISA 2017, EMSLIBS 2017. , Pisa .

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**Congress Center – Pisa, Italy**  
Pisa, 11<sup>th</sup>-16<sup>th</sup> of June 2017



**CSI XL - IX EMSLIBS**  
*Book of Abstracts*





*Book of Abstracts*  
**Congress Center Pisa, Italy**  
Pisa 11<sup>th</sup>-16<sup>th</sup> of June 2017

[www.csi-conference.org](http://www.csi-conference.org)  
[www.emslibs.org](http://www.emslibs.org)

## SCIENTIFIC ORGANIZATION



CNR-ICCOM

Institute for the Chemistry of OrganoMetallic Compounds

Area della ricerca CNR  
Via G. Moruzzi, 1 - 56124 Pisa  
Phone: (+39) 050 315.2552 / 2221  
Fax (+39) 050 315.2555 / 2553  
segreteria-pi@pi.iccom.cnr.it

## MANAGEMENT:



Asti Incentives & Congressi srl A.I.C.  
P.zza S. Uomobono, 30 - 56126 Pisa  
Phone #1 (+39) 050 598.808  
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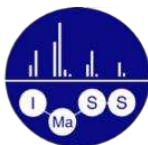
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## *Welcome Letter*

Dear participant of the CSI XL and IX EMSLIBS,

It is a great pleasure for the organizers to host the Colloquium Spectroscopicum Internationale XL and the IX Euro-Mediterranean Symposium on Laser Induced Breakdown Spectroscopy in Italy from 11<sup>th</sup> to 16<sup>th</sup> of June, 2017. It is the third time that both CSI and EMSLIBS are organized in Italy after the CSI II (Venice, 1951), CSI XVII (Florence, 1973), 5<sup>th</sup> EMSLIBS (Frascati, 2009) and 7<sup>th</sup> EMSLIBS (Bari, 2011). Since the first meeting in 1950, CSI was always a forum where scientists involved in all aspects of Spectroscopy meet to share their experience, discuss results and applications, and present new ideas. On the other hand, recent EMSLIBS conferences have transcended their original regional scope and acquired a global reputation, which will be enhanced this year by being co-organized with the Colloquium Spectroscopicum Internationale. Together these events represent a historic forum to discuss developments in fundamentals and applications of all branches of spectroscopy. The joint organization of the CSI and EMSLIBS events in Pisa has been realized with the aim to have a positive impact on both conferences by fostering synergisms among participants of all ages, as well as the level of participation, in the stimulating atmosphere of a beautiful city of art in Tuscany. We are grateful to the invited, plenary and keynote speakers, who agreed to contribute with their knowledge to the success of the conference, to all the participants presenting oral and poster contributions and to the sponsors for their generous support.

A special thanks to the people of Organizing, Scientific and Local Committees for their great work and effort, which has been indispensable for the organization of the CSI XL and IX EMSLIBS

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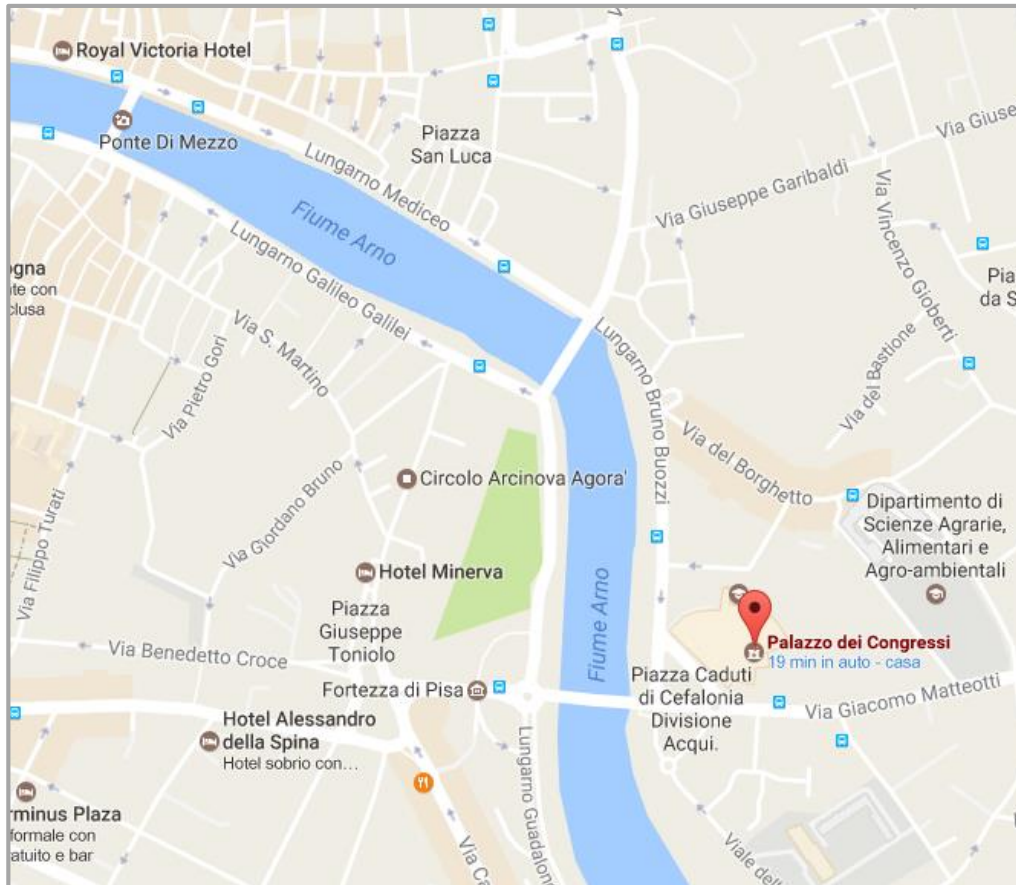
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For pre/post conference touristic information and assistance please contact Asti Incentives & Congressi srl (A.I.C.) at:

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# General Information

## Lectures and Oral Presentations

Plenary Lectures (PL) duration will be 45 min including discussion, Invited Lectures (IL) and Keynote Lectures (KL) will be 30 min including discussion, Oral Presentations (OP) will be 15 min, including discussion. All speakers are kindly asked to respect the time at their disposal in order to avoid any delay. The files for oral presentations should be saved in the following formats: Power Point Presentation (\*.ppt or \*.pptx) or PDF. Different formats might be incompatible with the presentation software provided by the Congress Center. All the presentations must be loaded on the main server of the Congress Center. Personal computers cannot be connected to the server.

Morning speakers are kindly requested to provide their presentation on USB the day before their lecture is scheduled. Afternoon speakers are kindly requested to provide their presentation on USB before the lunch break.

## ID Badge

For security reasons, the participants are requested to wear their ID badge during all the conference activities, including the social events.

## WIFI access

To access the Internet using WIFI, participants are encouraged to connect to the EDUROAM network, using their personal credentials. Alternatively, a personal password for free WIFI access can be obtained from the Conference desk, after presentation of a valid ID.

## Poster sessions

Posters should be mounted in the morning of the day on which they are scheduled and should be removed in the evening, no later than 8 pm.

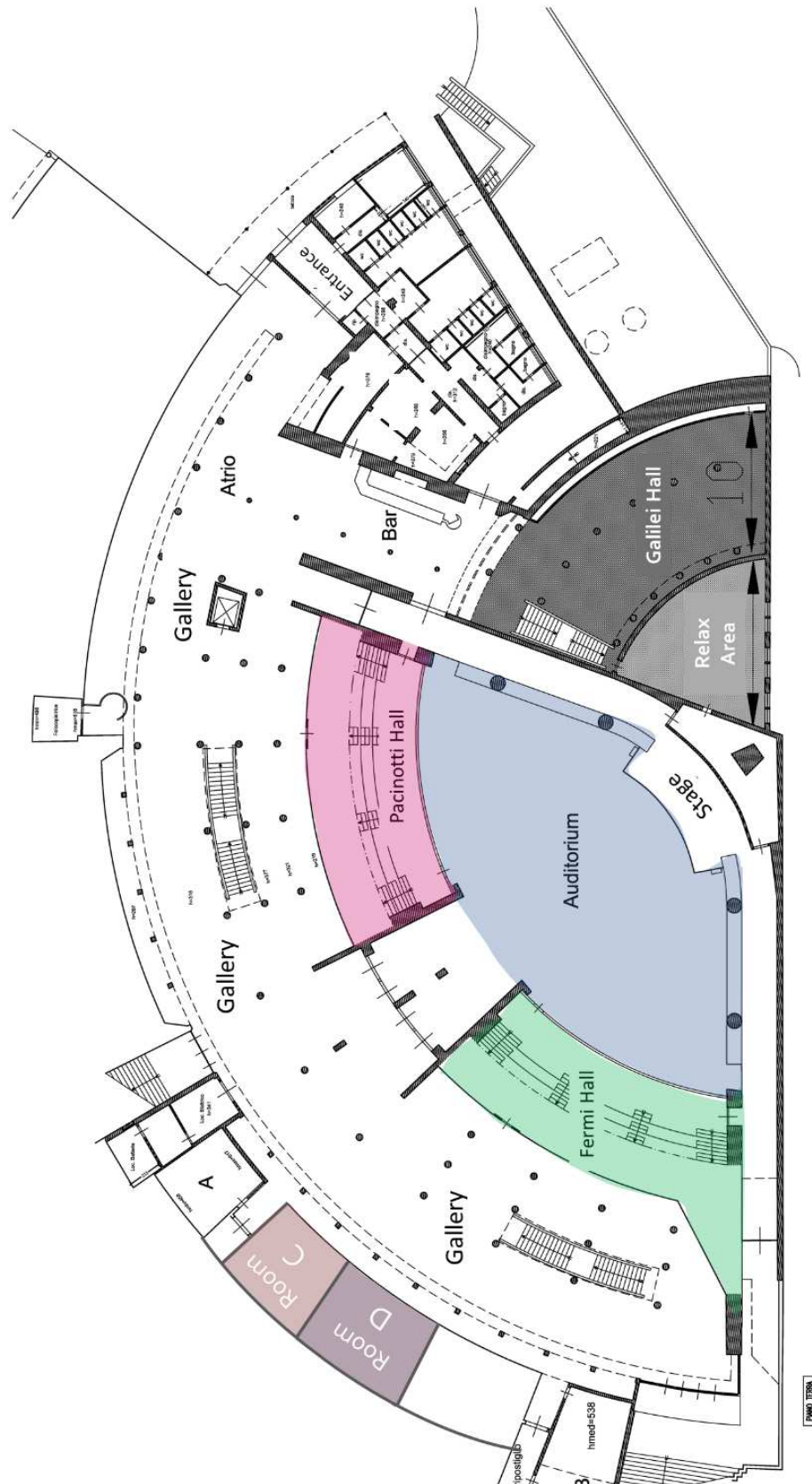
Supplies for mounting posters can be collected at the registration desk. Each poster will be assigned a board with a code corresponding to the one reported in this booklet.

Any posters left at the end of the poster session will be removed by the staff and discarded.

Presenting authors are encouraged to attend to their posters during the poster sessions to discuss the contents with other delegates.

Prizes for the Best Poster presented by a student are kindly sponsored by JAAS and Elsevier.

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# Synthetic Programme

MON					
8.30					
9.00	PLENARY LECTURE: Javier Laserna PL-01				
	Nanotech I	Food Analysis I	Archaeology and Cultural Heritage I	Environment I	Fundamentals of LIBS I
9:45	Goenaga IL-01	Sezer OL-10	Fantoni IL-04	Smichowski KL-04	Parigger IL-06
10:00		Boschetti OL-11			
10:15	Czaderna OL-01	Fernandez-Menendez OL-12	Pelosi KL-02	Campanella OL-38	Gasior OL-51
10:30	Bozkurt OL-02	Gomez-Nieto OL-13		GIOTTO BIOTECH Gentili OL-39	Alvarez-Llamas OL-52
	Nanotech II	Food Analysis II	Archaeology and Cultural Heritage II	Environment II	Fundamentals of LIBS II
11:15	Tugarova IL-02	Temiz OL-14	Cartechini OL-27	Urrutia-Goyes OL-40	Hermann KL-05
11:30		McCrindle OL-15	Gallello OL-28	Nunome OL-41	
11:45	Resano KL-01	Ercioglu OL-16	Rosi OL-29	Vassileva OL-42	Colonna OL-54
12:00		SHIMADZU Oppermann OL-17	Khramchenkova OL-30	Krata OL-43	IBSEN Rasmussen OL-55
12:15	Filipczak OL-03	Gonzalez-Cabrera OL-18	Wagner OL-31	Baysal OL-44	Lebedev OL-56
12:30	Matczuk OL-04	Chiba OL-19	Chieli OL-32	Wu OL-45	Safi OL-57
12:45	Ditaranto OL-05	Consumi OL-20		Li OL-46	
14.00	PLENARY LECTURE: Marco A. Zezzi Arruda PL-02				
	Nanotech III	Food Analysis III	Archaeology and Cultural Heritage III	Geological Applications I	Fundamentals of LIBS III
14:45	Karydas IL-03	Guyen OL-21	Bonaduce KL-03	Harmon IL-05	Aragon KL-06
15:00		Bierla OL-22			
15:15	Godlewska-Zylkiewicz OL-06	Ozbek OL-23	Spoto OL-34	Day OL-47	Houssyen OL-58
15:30	Pereira Leite OL-07	Comino OL-24	Cortea OL-35	Al-Rifai OL-48	Deguchi OL-59
15:45		Ranulfi OL-25	Columbu OL-36	Akhmetzhanov OL-49	Alwahabi OL-60
16:00				Pagnotta OL-50	Nosrati Ghods OL-61
16:15	COFFEE BREAK				

<b>TUE</b>					
<b>8.30</b>	PLENARY LECTURE: <b>Ove Axner PL-03</b>				
	<i>Industrial Applications I</i>	<i>Bio-medical Applications I</i>	<i>Geological Applications II</i>	<i>Archaeology and Cultural Heritage IV</i>	<i>Fundamentals of LIBS IV</i>
<b>9.15</b>	<b>El Hassan IL-07</b>	<b>Mizaikoff IL-08</b>	Kaski OL-94	<b>Manso KL-11</b>	<b>Gormushkin KL-13</b>
<b>9.30</b>			Hark OL-95		
<b>9.45</b>	François OL-62	<b>Hayden KL-08</b>	Senesi OL-96	Artesani OL-113	Carrasco-Garcia OL-126
<b>10.00</b>	Brogly OL-63		Schröder OL-97	Lucejko OL-114	Dietz OL-127
<b>10.15</b>	Connemann OL-64	Moncayo OL-79	Raneri OL-98	Catelli OL-115	Delaney OL-128
<b>10.30</b>	Eto OL-65	Lau OL-80	Harmon OL-99	Tempesta OL-116	Kramida OL-129
<b>10.45</b>					
	<i>Industrial Applications II</i>	<i>Bio-medical Applications II</i>	<i>LIBS &amp; Raman</i>	<i>Archaeology and Cultural Heritage V</i>	<i>Coal and Steel Analysis</i>
<b>11.15</b>	<b>Pershin KL-07</b>	<b>Kamnev KL-09</b>	<b>Angel KL-10</b>	<b>Carvalho IL-09</b>	<b>Z. Wang IL-11</b>
<b>11.30</b>					
<b>11.45</b>	Piorek OL-66	Alli OL-81	B&W TEK Li OL-100	Orsini OL-117	Pedarnig OL-130
<b>12.00</b>	SHIMADZU Knoop OL-67	Armanetti OL-82	Pavlov OL-101	Hassanimatin OL-118	Monfort OL-131
<b>12.15</b>	UI Haq OL-68	Gianoncelli OL-83	Bhatt OL-102	RENISHAW Tagliapietra OL-119	Cui OL-132
<b>12.30</b>	Zehra OL-69	Cheriet OL-84	AVANTES Otten OL-103	Idjouadiene OL-120	Sturm OL-133
<b>12.45</b>	Morillas OL-70	Zhang OL-85	Lednev OL-104	Shaykhutdinova OL-121	SCIAPS Day OL-134
<b>13.00</b>	Breithaupt OL-71				Mketo OL-135
<b>13.15</b>					
<b>14.15</b>	PLENARY LECTURE: <b>Montserrat Filella PL-04</b>				
	<i>Industrial Applications III</i>	<i>Bio-medical Applications III</i>	<i>Materials I</i>	<i>Speciation</i>	<i>LIBS imaging</i>
<b>15.00</b>	Fricke-Begemann OL-72	Signour OL-87	Moravkova OL-106	<b>Szpunar IL-10</b>	<b>Motto-Ros KL-14</b>
<b>15.15</b>	LTB Mory OL-73	Iaquinta OL-88	Lehmann OL-107		
<b>15.30</b>	Banerjee OL-74	Kanicky OL-89	Buzanich OL-108	<b>Lobinski KL-12</b>	ELEMISSION Doucet OL-136
<b>15.45</b>	Wilsh OL-75	Kalambuka OL-90	Virtanen OL-109		Gottlieb OL-137
<b>16.00</b>		Flori OL-91	X. Zhang OL-110	Matousek OL-123	Lazic OL-138
<b>16.15</b>			Berenji OL-111	Nyaba OL-124	Weimerskirch OL-139
<b>16.30</b>				Nawrocka OL-125	Požizka OL-140

<b>WED</b>					
<b>8.30</b>	PLENARY LECTURE: <b>Chris Le PL-05</b>				
	<i>Materials II</i>	<i>Proteomics</i>	<i>Food Analysis IV</i>	<i>Fuels</i>	<i>Liquid Analysis</i>
<b>9:15</b>	Jiang OL-141	<b>Bischoff IL-12</b>	Bilge OL-157	<b>Flores KL-20</b>	<b>Hidalgo KL-22</b>
<b>9:30</b>	Oztoprak OL-142		Varão Silva OL-158		
<b>9:45</b>	Giurlani OL-143	<b>Q. Wang KL-16</b>	Caceres OL-159	Jodlowski OL-163	Villagrán-Muniz OL-173
<b>10:00</b>	Jędrzejczyk OL-144		Piston OL-160	Sanchez-Rodriguez OL-164	Yalcin OL-174
<b>10:15</b>	Runka OL-145	Pereiro OL-153	Manzoor OL-161	Kowalewska OL-165	Ruiz Espinar OL-175
<b>10:30</b>		Rodríguez-Menéndez OL-154	Rico Rodríguez OL-162		Ripoll OL-176
	<i>Atomic Spect.</i>	<i>Forensic Applications</i>	<i>Vapor generation</i>	<i>Chemometrics</i>	
<b>11:15</b>	<b>de Loos-Vollebregt KL-15</b>	<b>Kawai KL-17</b>	<b>Dedina KL-21</b>	<b>Sirven KL-23</b>	
<b>11:30</b>					
<b>11:45</b>	Borges OL-147	<b>Sabbatini KL-18</b>	Pagliano OL-167	Devangad OL-177	
<b>12:00</b>	Zhu OL-148		Kratzer OL-168	Hwang OL-178	
<b>12:15</b>	AGILENT Scardina OL-149	<b>Schechter KL-19</b>	Marschner OL-169	Onkangi N. Joshua OL-179	
<b>12:30</b>	Muniz OL-150		Schram OL-170	Diaz OL-180	
<b>12:45</b>	Temuge OL-151	Yang OL-155	Wagatsuma OL-171		
<b>13:00</b>	ATOMTRACE Klus OL-152	Kotrly OL-156			

THU				
8:30	PLENARY LECTURE : Annemie Bogaerts PL-06			
	<i>Geological Applications III</i>	<i>Environment III</i>	<i>Clinical and Pharma I</i>	<i>Underwater LIBS</i>
9:15	Sabsabi IL-13	Mester KL-25	Gaudio IL-19	Sakka KL-28
9:30				
9:45	Rammelkamp OL-183	Lesniewska OL-193	Liang OL-205	Thornton OL-221
10:00	Frydenvang OL-184	Mihucz OL-194	Bellagambi OL-206	Yoshino OL-222
10:15	Schneider OL-185	Rezk OL-195	Mesko OL-207	Dell'Aglio OL-223
10:30	Oshtrakh OL-186	LUMEX Ivanov OL-196		Takahashi OL-224
	<i>Fundamentals of Mass Spectrometry</i>	<i>Environment IV</i>	<i>Clinical and Pharma II</i>	
11:15	Careri IL-14	Viljanen OL-197	Chwiej OL-209	Mini theoretical / practical course on XRF and Raman XGLAB
11:30		Wang OL-198	Alenkina OL-210	
11:45	Bulska KL-24	Capobianco OL-199	Ustabasi OL-211	
12:00		Renner OL-200		
12:15	PERKIN ELMER Stephan OL-187			
12:30	PLENARY LECTURE: Rick Russo PL-07			
	<i>Computational Spectroscopy</i>	<i>Nuclear Applications</i>	<i>Clinical and Pharma III</i>	<i>Nano-LIBS</i>
14:15	Barone IL-15	M. Martin IL-17	Di Francesco KL-27	De Giacomo KL-29
14:30				
14:45	Záliš IL-16	R. Martin IL-18	Pessanha OL-214	Sanchez-Ake IL-20
15:00			Lomonaco OL-215	
15:15	Baiardi OL-188	Colao KL-26	Jeong OL-216	Semerok OL-225
15:30	Pardini OL-189		Živković OL-217	Poggialini OL-226
15:45	Zanetti Polzi OL-190	Myhre OL-202	Miliszewicz OL-218	El Sherbini OL-227
16:00	Guerra OL-191	Wabwile OL-203		Eseller OL-228
16:15	Fusè OL-192	Veis OL-204		Pacheco OL-229

<b>FRI</b>	
<b>8.30</b>	<p>CSI AWARD CEREMONY</p> <p>AWARD LECTURE: <b>Bernhard Welz</b></p>
<b>9.30</b>	<p>EMSLIBS AWARD CEREMONY</p> <p>AWARD LECTURE: <b>Nico Omenetto</b></p>
<b>10.30</b>	<p>COFFEE BREAK</p>
<b>11.00</b>	<p>JAAS-EIL Award Lecture: <b>Sohail Mushtaq</b></p>
<b>11:45</b>	<p>OSA Lecture: <b>Mohamed Abdel Harith</b></p>
<b>12:15</b>	<p>POSTER AWARDS CEREMONY</p>
<b>12:30</b>	<p>ANNOUNCEMENT OF NEXT CSI XLI AND XLII / 10<sup>th</sup> EMSLIBS</p> <p>PRESENTATION CSI XLI</p> <p>CLOSING CEREMONY</p>



## SESSIONS' CHAIRS & ROOMS

### Monday, 12<sup>th</sup> June

#### Morning

9:00 – PL01 – Javier Laserna (Chair- V. Palleschi), Auditorium

Session – Time – 9:45-10:45	Chairperson	Room
Nanotech I	A. Karydas	C
Food Analysis I	M. Resano	D
Archaeology e Cultural Heritage I	I. Bonaduce	Pacinotti
Environment I	E. Bulska	Fermi
Fundamentals of LIBS I	J. Hermann	Auditorium
Session – Time – 11:15-13:00	Chairperson	Room
Nanotech II	H. Goenaga-Infante	C
Food Analysis II	M. Goreti	D
Archaeology e Cultural Heritage II	F. Modugno	Pacinotti
Environment II	P. Smichowski	Fermi
Fundamentals of LIBS II	C. Parigger	Auditorium

#### Afternoon

14:00 – PL02 – Marco Arruda (Chair – A. D'Ulivo), Auditorium

Session – Time – 14.45-16:00	Chairperson	Room
Nanotech III	A. Tugarova	C
Food Analysis III	D. Borges	D
Archaeology e Cultural Heritage III	L. Carvalho	Pacinotti
Geological Applications I	J. Dědina	Fermi
Fundamentals of LIBS III	C. Parigger	Auditorium

## Tuesday, 13th June

### Morning

8:30 – PLo3 – Ove Axner (Chair- J. Laserna), Auditorium

Session – Time – 9:15-10:45	Chairperson	Room
Industrial Applications I	M. Martin	C
Biomedical Applications I	R. Lobinski	D
Geological Applications II	R. Harmon	Fermi
Archaeology e Cultural Heritage IV	R. Fantoni	Pacinotti
Fundamentals of LIBS IV	Z. Wang	Auditorium
Session – Time – 11:15-13:15	Chairperson	Room
Industrial Applications II	A. El Hassan	C
Biomedical Applications II	B. Mizaikoff	D
Archaeology e Cultural Heritage V	L. Sabbatini	Pacinotti
LIBS & Raman	V. Lazic	Fermi
Coal & Steel Analysis	R. Martin	Auditorium

### Afternoon

14:15 – PLo4 – Montserrat Filella (Chair- Chris Le), Auditorium

Session – Time – 15:00-16:15	Chairperson	Room
Industrial Applications III	S. Pershin	C
Biomedical Applications III	G. Spoto	D
Materials I	J. Kawai	Pacinotti
Speciation	Q. Wang	Fermi
LIBS Imaging	M. Angel	Auditorium

## Wednesday, 14<sup>th</sup> June

### Morning

8:30 – PLo5 – Chris Le (Chair- M. Filella), Auditorium

Session – Time – 9:15-10:45	Chairperson	Room
Materials II	N. Ditaranto	Pacinotti
Proteomics	J. Szpunar	C
Food Analysis IV	M. Careri	D
Fuels	T. Matousek	Fermi
Liquid Analysis	S. Legnaioli	Auditorium
Session – Time – 11:15-13:15	Chairperson	Room
Atomic Spectroscopy	V. Kanicky	Pacinotti
Forensic Applications	Z. Kowalewska	C
VG & Sample Introduction	E. Flores	Fermi
Chemometrics	A. De Giacomo	Auditorium

## Thursday, 15<sup>th</sup> June

### Morning

8:30 – PLo6- Annemie Bogaerts (Chair- M. de Loos-Vollebregt), Auditorium

Session – Time – 9:15-10:45	Chairperson	Room
Geological Applications III	S. Kaski	Fermi
Environment III	I. Schechter	D
Clinical and Pharma II	R. Bischoff	Pacinotti
Underwater LIBS	M. Hidalgo	Auditorium
Session – Time – 11:15-12:30		Room
Fundamentals of Mass Spectrom.	M. Arruda	Fermi
Environment IV	Z. Mester	D
Clinical and Pharma II	J. Caceres	Pacinotti
Practical Course XRF & Raman	R. Alberti	C

### Afternoon

14:00 – PLo7 – Rick Russo (Chair –V. Palleschi), Auditorium

Session – Time – 14.15-16:30	Chairperson	Room
Computational Spectroscopy	A. Kamnev	Fermi
Nuclear Applications	J.B. Sirven	D
Clinical and Pharma	A. Raffaelli	Pacinotti
Nano-LIBS	R. Gaudioso	Auditorium

## Friday, 16<sup>th</sup> June

### Morning, Auditorium

Chairpersons: A. D'Ulivo, V. Palleschi, S. Legnaioli

## Detailed Scientific Programme

Sunday	Monday					Tuesday				
	Welcome to the Participants (8:30-9:00) Auditorium					Plenary Lecture PL 03 (8:30-9:15) Ove Axner- Auditorium				
	Plenary Lecture PL 01 (9:00-9:45) Javier Laserna - Auditorium									
	9:45-10:45 Nanotech I Room C	9:45-10:45 Food Analysis I Room D	9:45-10:45 Arch&Heritage I Pacinotti Hall	9:45-10:45 Envir I Fermi Hall	9:45-10:45 LIBS I Auditorium	9:15-10:45 Industrial I Room C	9:15-10:30 Biomed I Room D	9:15-10:45 Geo II Fermi Hall	9:15-10:45 Arch&Heritage IV Pacinotti Hall	9:15-10:45 LIBS IV Auditorium
	Coffee Break (10:45-11:15, 30min)					Coffee Break (10:45-11:15, 30min)				
	11:15-13:00 Nanotech II Room C	11:15-13:00 Food Analysis II Room D	11:15-13:00 Arch&Heritage II Pacinotti Hall	11:15-13:00 Envir II Fermi Hall	11:15-13:00 LIBS II Auditorium	11:15-13:15 Industrial II Room C	11:15-13:00 Biomed II Room D	11:15-13:00 LibsRaman Fermi Hall	11:15-13:00 Arch&Heritage V Pacinotti Hall	11:15-13:15 Coal&Steel Auditorium
	Lunch (13:00-14:00, 60min)					Lunch (13:15-14:15, 60min)				
	Plenary Lecture PL 02 (14:00-14:45) Marco A. Zezzi Arruda - Auditorium					Plenary Lecture PL 04 (14:15-15:00) Montserrat Filella- Auditorium				
	14:45-16:00 Nanotech III Room C	14:45-16:00 Food Analysis III Room D	14:45-16:00 Arch&Heritage III Pacinotti Hall	14:45-16:15 Geo I Fermi Hall	14:45-16:15 LIBS III Auditorium	15:00-16:15 Industrial III Room C	15:00-16:15 Biomed III Room D	15:00-16:30 Materials I Pacinotti Hall	15:00-16:45 Speciation Fermi Hall	15:00-16:45 Libs Imaging Auditorium
	Coffee Break (16:15-16:45, 30 min)					Coffee Break (16:45-17:15, 30 min)				
Registration 17:15-19:00	Poster Session I (17:00-18:30)					Poster Session II (17:30-19:00)				
Welcome Cocktail 19:00-20:30	Wine Tasting (18:30-20:00)									
	CSI Delegates' Meeting (20:00)					Organ Concert (21:00)				

Wednesday					Thursday				Friday
Plenary Lecture PL 05 (8:30-9:15) Chris Le - Auditorium					Plenary Lecture PL 06 (8:30-9:15) Annemie Bogaerts - Auditorium				CSI AWARD Bernard Welz 8:30-9:30
9:15-10:45 Materials II Pacinotti Hall	9:15-10:45 Proteomics Room C	9:15-10:30 Food Analysis IV Room D	9:15-10:30 Fuels Fermi Hall	9:15-10:45 Liq. Analysis Auditorium	9:15-10:45 Geo III Fermi Hall	9:15-10:45 Envir III Room D	9:15-10:45 Pharma I Pacinotti Hall	9:15-10:45 Underwater LIBS Auditorium	LIBS AWARD Nicolo Omenetto 9:30-10:30
Coffee Break (10:45-11:15, 30min)					Coffee Break (10:45-11:15, 30min)				Coffee Break 10:30-11:00
11:15-13:15 Atom Spectr Pacinotti Hall	11:15-13:15 Forensic Room C	11:15-13:00 Vapor Generation Fermi Hall	11:15-12:45 Chemometrics Auditorium	11:15-12:30 Mass Spectr Fermi Hall	11:15-12:15 Envir IV Room D	11:15-12:00 Pharma II Pacinotti Hall	11:15-12:30 XRF-Raman Mini-Course Room C	JAAS-EIL AWARD Sohail Mushtaq 11:00-11:45	
								OSA Lecture Mohamed A. Harith 11:45-12:15	
								POSTER AWARDS	
								Announcement of CSI XLI and 10thEMSLIBS CLOSING 12:30-13:00	
Lunch (13:15-14:15, 60min)					Lunch (12:30-13:30, 60min)				
Visit of Pisa (14:30-18:00)					Plenary Lecture PL 07 (13:30-14:15) Rickard Russo- Auditorium				
					14:15-16:30 CompChem Fermi Hall	14:15-16:30 Nuclear App Room D	14:45-16:00 Pharma III Pacinotti Hall	14:45-16:30 NanoLibs Auditorium	
					Coffee Break (16:30-17:00, 30min)				
					Poster Session III (17:15-18:45)				
									“Luminara” Fireworks 21:00
Social Dinner (20:00)					EMSLIBS Scientific Committee Meeting (20:00)				



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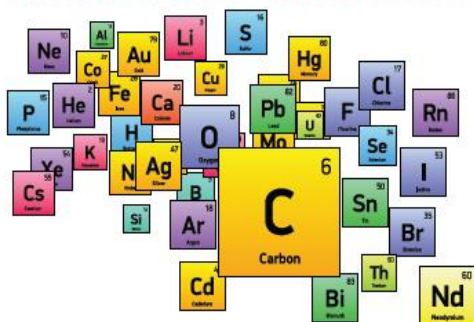
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## Plenary Lectures

### Monday 12<sup>th</sup> of June

**PLo1 Javier Laserna** (Universidade de Malaga, Spain) *The sources, progress and frontiers of an exciting technology: laser-induced breakdown spectroscopy*

**PLo2 Marco A. Zezzi Arruda** (University of Campinas, Brasil) *Unraveling genetically modified organisms through mass spectrometry*

### Tuesday 13<sup>th</sup> of June

**PLo3 Ove Axner** (Umeå University, Sweden) *NICE-OHMS and NICE-AAS - Frequency Modulated Cavity Enhanced Spectroscopic Techniques for Sensitive Detection of Molecules and Atoms down to  $10^{-14}$  cm<sup>-1</sup>. Principles, Current Status, and Prospects*

**PLo4 Filella Montserrat** (University of Geneva, Switzerland) *When Anthropocene means exploiting all the elements of the periodic table: a new challenge for environmental analytical chemistry*

### Wednesday 14<sup>th</sup> of June

**PLo5 X. Chris Le** (University of Alberta, Canada) *Arsenic Speciation and Arsenic Binding to Proteins*

### Thursday 15<sup>th</sup> of June

**PLo6 Annemie Bogaerts** (University of Antwerp, Belgium) *The plasma characteristics and sample behavior in the ICP revealed through computer modeling*

**PLo7 Richard E. Russo** (University of Berkeley, California USA) *Solid Matrix Transformation as a Sample Preparation Method for Laser Induced Breakdown Spectroscopy and Laser Ablation Inductively Coupled Plasma Analysis*

## Awards

### Friday 16<sup>th</sup> of June

**CSI Award: Bernard Welz** (Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis, SC, Brazil) *Solid Matrix High-resolution Continuum Source Absorption Spectrometry can do it...*

**LIBS Award: Nicolo Omenetto** (University of Florida, Gainesville, FL, USA) *Laser Induced breakdown spectroscopy: personal reminiscences of a long lasting interaction*

**JAAS-EIL Award: Sohail Mushtaq** (London Metropolitan University, United Kingdom) *Latest developments in understanding the plasma processes in analytical glow discharge optical emission and mass spectrometry*

**OSA Lecture: Mohamed Abdel Harith** (University of Cairo, Egypt) *Evolution of EMSLIBS from regional meeting to an inclusive global event*



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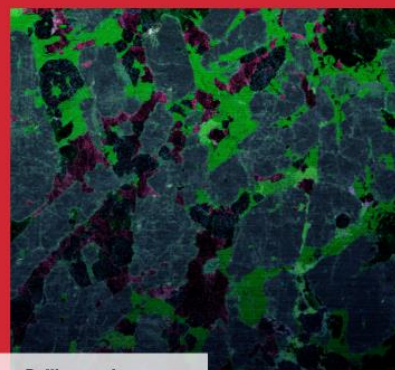


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## Nanotech Sessions

### Nanotech I – Monday 12<sup>th</sup> of June – Early Morning Session

- (09.45–10.15) **IL01** Invited Lecture: **Heidi Goenaga**, S. Nunez, D. Bartczak *QQQ ICP–MS hyphenations for the characterizations of manufactured nanomaterials in complex matrices: from sized based speciations to counting*  
 (10.15–10.30) **OL01–Anna Czaderna**, M. Kozanecki, M. Makowski, J. Tyczkowski *The feasibility of analysis of water structure in electric field using molecular spectroscopies*  
 (10.30–10.45) **OL02–Akif G. Bozkurt**, G. G. Büyükgöz A, M. Şöforoğlu A, Uğur Tamer B, İ. H. Boyacı *Alkaline phosphatase labeled SERS active sandwich immunoassay for the detection of E. coli*

### Nanotech II – Monday 12<sup>th</sup> of June – Late Morning Session

- (11.15–11.45) **IL02** Invited Lecture: **Anna V. Tugarova**, A. A. Kamnev *Vibrational Spectroscopy in Studying Microbially Synthesised Selenium Nanoparticles*.  
 (11.45–12.15) **KL01** Keynote Lecture: **Martin Resano**, E. García–Ruiz, R. Garde *Characterization of metallic nanoparticles via high resolution continuum source atomic absorption spectrometry*  
 (12.15–12.30) **OL03–Paulina Filipczak**, M. Kozanecki, K. Halagan *Surface Enhanced Raman Scattering of Water in Dispersions of Silver Nanoparticles*  
 (12.30–12.45) **OL04–Magdalena Matczuk**, J. Legat *CE–ICP–MS as a platform to differentiate the speciation changes of various therapeutic metal nanomaterials in human serum*  
 (12.45–13.00) **OL05–Nicoletta Ditaranto**, M. C. Sportelli, R. A. Picca, L. Sabbatini, N. Cioffi *Spectroscopic characterization of second-generation nanostructured antimicrobials*

### Nanotech III – Monday 12<sup>th</sup> of June – Afternoon Session

- (14.45–15.15) **IL03** Invited Lecture: **Andreas–Germanos Karydas**, M. Czyzycki, A. Migliori, J. J. Leani, J. Osan, N. Vakula, M. Bogovac, P. Wrobel, I. Darby, R. B. Kaiser *Interdisciplinary synchrotron radiation based X-ray spectrometry applications using the IAEA multi-technique instrument operated at the XRF beamline of Elettra Sincrotrone Trieste*.  
 (15.15–15.30) **OL06–Beata Godlewska–Żyłkiewicz**, J. Malejko, N. Świerżewska *Development of HPLC–ICP MS Method for Separation and Determination of Nano and Ionic Forms of Gold and Silver*  
 (15.30–15.45) **OL07–Diego Pereira Leite**, E. Bolea–Fernandez, A. Rua–Ibarz, M. Resano, F. Vanhaecke, M. Aramendía *Characterization of SiO<sub>2</sub> Nanoparticles by Single Particle – Inductively Coupled Plasma – Tandem Mass Spectroscopy*

## Food Analysis Sessions

### Food Analysis I – Monday 12<sup>th</sup> of June – Early Morning Session

- (09.45–10.00) **OL10–Banu Sezer**, G. Bilge, İ. H. Boyacı *Laser Induced Breakdown Spectroscopy Based Protein Assay for Cereal Samples*  
 (10.00–10.15) **OL11–William Boschetti**, L. M. G. Dalagnol, M. B. Dessuy, M. Dullius, M. Goretti, R. Vale *Control of spectral interference in must and wine analysis via high-resolution continuum source flame atomic absorption spectrometry*  
 (10.15–10.30) **OL12–Sonia Fernández–Menéndez**, R. R. Alves Peixoto, M. L. Fernández–Sánchez, B. Fernández–Colomer, M. Suarez, M. Costa, A. Sanz–Medel *Elemental mass spectrometric evaluation of iron nanoparticles as an enhanced iron supplement for formula milk*  
 (10.30–10.45) **OL13–Beatriz Gómez–Nieto**, L. Fernández–López, M. J. Gismera, T. Sevilla, J. R. Procopio *Evaluation of internal standardization to improve the determination of trace elements in beverages by high-resolution continuum source flame atomic absorption spectrometry*

### Food Analysis II – Monday 12<sup>th</sup> of June – Late Morning Session

- (11.15–11.30) **OL14–Havva Tumay Temiz**, B. Sezer, A. Berkkan, İ. H. Boyacı *Laser Induced Breakdown Spectroscopy for Determination of Butter Adulteration*  
 (11.30–11.45) **OL15–Rob McCrindle**, B. Mehari, M. Redi–Abshiro, B. S. Chandravanshi, S. Combrinck *Identification of the Region of Cultivation of Ethiopian Coffee Using Spectrometric Data*  
 (11.45–12.00) **OL16–Elif Ercioglu**, S. D. Velioglu, H. T. Temiz, H. M. Velioglu, A. Topcu, İ. H. Boyacı *Barcoding Approach for Determination of Vegetable Oil by Raman Spectroscopy*  
 (12.00–12.15) **OL17–(SHIMADZU)–Uwe Oppermann** *Wine Analysis by ICPMS–2030*  
 (12.15–12.30) **OL18–Maria González–Cabrera**, A. Domínguez–Vidal, M. J. Ayora–Cañada *Study of olive fruit ripening process by means of principal component analysis of hyperspectral FTIR images*  
 (12.30–12.45) **OL19–Koichi Chiba**, T. Iwai, T. Narukawa *Arsenic Speciation and Cadmium Determination in Tobacco Leaves and Smoke*  
 (12.45–13.00) **OL20–Marco Consumi**, G. Leone, G. Tamasi, C. Bonechi, C. Rossi, A. Magnani *High quality analysis of food by multivariate ToF–SIMS*

*Food Analysis III – Monday 12<sup>th</sup> of June – Afternoon Session*

(14.45–15.00) **OL21–Burcu Guven**, E. A. Soykut, I. H. Boyaci, U. Tamer *Developing the Rolling Circle Amplification (RCA) Based Surface-Enhanced Raman Spectroscopy (SERS) Method for Genetically Modified Organisms (GMOs)*

(15.00–15.15) **OL22–Katarzyna Bierla**, J. Jimenez-Lamana, J. Szpunar, R. Lobinski *Selenocysteine and selenium nanoparticle determination in selenium-rich yeast by coupled techniques and single particle ICP MS*

(15.15–15.30) **OL23–Nil Ozbek**, S. Akman *Application of Solid Sampling for the Determination of Total Fluorine in Some Fish Varieties and Other Seafoods by High-Resolution Continuum Source Graphite Furnace Molecular Absorption Spectrometry*

(15.30–15.45) **OL24–Francisco Comino**, A. Domínguez-Vidal, M. J. Ayora-Cañada, V. A. Sanjuán *Near infrared spectroscopy and X-ray fluorescence data fusion for olive nutritional status determination*

(15.45–16.00) **OL25–Anielle Coelho Ranulfi**, G. S. Senesi, J. B. Caetano, M. C. Meyer, A. B. Magalhães, Paulino R. Villas-Boas, Débora M. B. P. Milori *Nutritional characterization by laser-induced breakdown spectroscopy of healthy and *Aphelenchoides* sp. Infected soybean leaves*

*Food Analysis IV – Wednesday 14<sup>th</sup> of June – Early Morning Session*

(09.15–09.30) **OL157–Gonca Bilge**, B. Sezer, I. H. Boyaci *Comparison of Laser Induced Breakdown Spectroscopy Analysis Between Milk and Milk Powder*

(09.30–09.45) **OL158–Tiago Varão Silva**, J. A. Gomes Neto, D. M. B. P. Milori, E. J. Ferreira, E. C. Ferreira *Quantitative prediction of coffee adulteration by defective beans using Laser-Induced Breakdown Spectroscopy*

(09.45–10.00) **OL159–Jorge Caceres**, S. Manzoor, S. Moncayo, D. Rosales, R. Izquierdo-Hornillos, J. Anzano *Food analysis by Laser Induced Breakdown Spectroscopy (LIBS)*

(10.00–10.15) **OL160–Mariela Pistón**, S. Mondutey, I. Machado, N. Pastorino, V. Arce, F. Iaquinta *Determination of Cu, Fe, Mn and Zn in wheat flour using TXRF: Comparison with FAAS and ETAAS*

(10.15–10.30) **OL161–Sadia Manzoor**, S. Moncayo, J. D. Rosales, R. Izquierdo, J. Anzano, J. O. Caceres *Qualitative and quantitative analysis of milk for the detection of adulteration by Laser Induced Breakdown Spectroscopy*

(10.30–10.45) **OL162–María del Carmen Rico Rodríguez**, S. Manzoor, J. D. Rosales, J. O. Cáceres *Fast Detection of Adulteration in Honey using Laser-Induced Breakdown Spectroscopy and Neural Networks*

**Archeology & Cultural Heritage Sessions***Arch&Heritage I – Monday 12<sup>th</sup> of June – Early Morning Session*

(09.45–10.15) **ILo4** Invited Lecture: **Roberta Fantoni** *In situ and remote spectroscopic characterization of Cultural Heritage surfaces*

(10.15–10.45) **KLo2–Claudia Pelosi**, G. Agresti, G. Bonifazi, G. Capobianco, F. Morresi, S. Rossi, U. Santamaria, S. Serranti *Multi-analytical approach for the evaluation of the stability of paint-ing materials for conservation purposes*

*Arch&Heritage II – Monday 12<sup>th</sup> of June – Late Morning Session*

(11.15–11.30) **OL27–Laura Cartechini**, D. Buti, F. Rosi, C. Anselmi, S. Centurioni, F. Talarico, G. Tranquilli, C. Zaccheo, C. Miliani *Chemical changes in oil paints containing copper-based green pigments: a systematic investigation by ATR-FTIR spectroscopy*

(11.30–11.45) **OL28–Gianni Gallelo**, J. Bernabeu, A. Diez, P. Escriba, A. Pastor, M. Lezzerini, M. E. Hodson, D. Stump *Rare Earth Elements analysis to identify anthropogenic signatures at the Valle del Serpis (Spain) Neolithic settlements*

(11.45–12.00) **OL29–Francesca Rosi**, M. Patti, E. Buzzegoli, R. Cremoncini, F. Gabrieli, L. Cartechini, R. Fontana, D. Kunzelman, A. Romani, C. Anselmi, D. Buti, B. G. Brunetti, A. Sgamellotti, C. Miliani *MOLAB transnational access at the Estorick Collection: non invasive study of the Italian Futurist paintings*

(12.00–12.15) **OL30–Rezida Khramchenkova**, P. Kaplan, A. Sitdikov, I. Biktagirova *Research of gesso and paint layers of the fresco painting of St. Christopher with a horse head from the Assumption Cathedral on the Sviyazhsk Island (Russia)*

(12.15–12.30) **OL31–Barbara Wagner**, L. Kępa, Z. Żukowska, A. Lewandowska *Screening of inorganic species using LA-ICP-MS imaging data and Raman spectroscopy for historic pigments identification*

(12.30–12.45) **OL32–Annalisa Chieli**, A. Romani, B. Doherty, C. Anselmi, I. Degano, F. Sabatini, C. Miliani *Why does Geranium lake fade? Photochemical study of eosin-based pigments in oil paints*

*Arch&Heritage III – Monday 12<sup>th</sup> of June – Afternoon Session*

(14.45–15.15) **KLo3** Keynote Lecture: **Ilaria Bonaduce** *Organic mass spectrometry to investigate molecular degradation phenomena of modern oil paintings*

(15.15–15.30) **OL34–Giuseppe Spoto**, G. Grasso, M. Calcagno, A. Rapisarda, R. D'Agata *Atmospheric pressure MALDI for the non-invasive characterization of carbonaceous ink from Renaissance documents*

(15.30–15.45) **OL35–Ioana Maria Cortea**, R. Rădvan, L. Gher vase, L. Ratoiu, M. Dinu *In-situ characterization of the pictorial layers of an original 1771 Pascal Taskin harpsichord*

(15.45–16.00) **OL36–Stefano Columbu**, S. Carboni, S. Pagnotta, M. Lezzerini, S. Raneri, S. Legnaioli, V. Palleschi *Secondary mineral phases and ancient treatments on limestone from Monte de Prama nuragic statues (Sardinia, Italy)*

**Arch&Heritage IV – Tuesday 13<sup>th</sup> of June – Early Morning Session**

- (09.15–09.45) **KL11** Keynote Lecture: **Marta Manso**, S. Pessanha, M. Guerra, J. P. dos Santos, M. L. Carvalho *X-ray fluorescence and Raman analytical techniques in written and artistic documents characterization*
- (09.45–10.00) **OL113–Alessia Artesani**, S. Mosca, A. Nevin, G. Valentini, D. Comelli *Time resolved photoluminescence spectroscopy for investigation of semiconductor modern pigments*
- (10.00–10.15) **OL114–Jeannette J. Lucejko**, J. La Nasa, C. M. A. McQueen, F. Modugno, S. Braovac, M. P. Colombini *Protective effect of linseed oil varnish on archaeological wood treated with alum*
- (10.15–10.30) **OL115–Emilio Catelli**, G. Sciutto, J. Yiming, S. Prati, R. Mazzeo *Total Reflection Near and Mid-Infrared Spectroscopic Studies on Outdoor and Archaeological Bronze Patinas*
- (10.30–10.45) **OL116–Gioacchino Tempesta** *Micro-LIBS vs. XRF analysis of surface-enriched silver coins. Is a micro-destructive approach really unavoidable?*

**Arch&Heritage V – Tuesday 13<sup>th</sup> of June – Late Morning Session**

- (11.15–11.45) **IL09** Invited Lecture: **Maria Luisa Carvalho**, M. Manso, S. Pessanha, A. Guilherme, I. Queralt *X-ray micro beam: Cultural and archaeological heritage applications overview*
- (11.45–12.00) **OL117–Sibilla Orsini**, F. Zinna, T. Biver, L. Di Bari, I. Bonaduce, M. P. Colombini *Spectroscopic investigation of the interactions between commercial stains and protein matrices used in paintings*
- (12.00–12.15) **OL118–Mohammadmahdi Hassanimatin**, S. H. Tavassoli, Y. N. Qhods, H. Nozari *Reducing Ablation and Improving Signal in Laser Induced Breakdown Spectroscopy by Using Spark Discharge in Sensitive and Valuable Samples*
- (12.15–12.30) **OL119–(RENISHAW)–Riccardo Tagliapietra** *The road map towards providing a robust Raman spectroscopy-based cancer diagnostic platform and integration into clinic*
- (12.30–12.45) **OL120–Lynda Idjouadiene** *The first study of non-destructive technical to some manuscripts of Algerian heritage.*
- (12.45–13.00) **OL121–Eugenia Shaykhutdinova**, R. Khranchenkova, R. Khasanov, A. Sitdikov *A unique 10th century silver coin of the Banijurid dynasty (Bolgar settlement, Russia)*

**Environment Sessions****Envir I – Monday 12<sup>th</sup> of June – Early Morning Session**

- (09.45–10.15) **KLo4** Keynote Lecture: **Patricia Smichowski**, F. Fujiwara, M. E. Guiñez, S. Cerutti, D. Gómez *Oxygenated and nitrated PAHs in the atmosphere of Buenos Aires. Determination by UHPLC(+)-APC-MS/MS*
- (10.15–10.30) **OL38–Beatrice Campanella**, L. Biancalana, C. Casiot, M. Onor, M. Perotti, R. Petrini, E. Bramanti *The feasibility of analysis of water structure in electric field using molecular spectroscopies*
- (10.30–10.45) **OL39–(GIOTTO BIOTECH)–Matteo Gentili**, A. Bonari, I. Pompilio, S. Dugheri *Customized reference compounds for the determination of pollutants, metabolites and residues of chemical manufacturing*

**Envir II – Monday 12<sup>th</sup> of June – Late Morning Session**

- (11.15–11.30) **OL40–Ricardo Urrutia-Goyes**, A. Argyraki, N. Ornelas-Soto *Compound Methodology for the Characterization of Lead Contamination in Soil: The Case of a Former Battery Factory in Monterrey, Mexico*
- (11.30–11.45) **OL41–Yoko Nunome**, K. Kodama, Y. Ueki, R. Yoshiie, I. Naruse, K. Wagatsuma *Detection of Volatile Organic Compounds in direct current pulse glow discharge plasma by Soft Plasma Ionization Mass Spectrometry*
- (11.45–12.00) **OL42–Emilia Vassileva**, I. Wysocka *Determination of selected trace elements in the open ocean*
- (12.00–12.15) **OL43–Agnieszka Anna Krata**, J. Karasinski, E. Bulska, M. Wojciechowski, L. Halicz *Ion Chromatography Coupled Multicollector/ICP MS in the Determination of Inorganic Cations*
- (12.15–12.30) **OL44–Asli Baysal**, H. Saygin, G. S. Ustabasi *Impact of soil and root type on the behavior of ZnO and Al<sub>2</sub>O<sub>3</sub> by microbial and antioxidant activity*
- (12.30–12.45) **OL45–Li Wu**, H.–S. Chae, A. Malek, H. Kim, C. Ro *Chemical compositional bulk analysis of size-segregated aerosol particles using ATR-FTIR*
- (12.45–13.00) **OL46–Xue Li**, J. Lee, H.–J. Eom, H.–J. Yoo, C.–U. Ro *Real-Time Investigation of Chemical Compositions and Hygroscopic Properties of Aerosols Generated from NaCl and Oxalic Acid Mixture Solutions Using in Situ Raman Microspectrometry*

**Envir III – Thursday 15<sup>th</sup> of June – Early Morning Session**

- (09.15–09.45) **KL25** Keynote Lecture: **Zoltan Mester**, P.–M. Le, J. Ding, D. M. Leek, J. Meija, G. Robertson, A. Windust, T. Matousek *Arsenic speciation in certified reference materials*
- (09.45–10.00) **OL193–Barbara Leśniewska**, B. Godlewska-Żyłkiewicz, L. Trzonkowska *Novel Methods for Speciation Analysis of Chromium in Environmental Samples Based on Solid Phase Extraction and Ion-exchange Chromatography Coupled to Atomic Spectrometry*
- (10.00–10.15) **OL194–Victor G. Mihucz**, L. Bencs, M. Óvári, C. Streli, G. Záray *A Simple Speciation Method for Monitoring Arsenic Removal from Drinking Water*

(10.15–10.30) **OL195–Reham Afifi Rezk** *LIBS and XRF analysis of heavy metals adsorbed in fish bones: Adsorption Isotherm and Kinetics Studies*

(10.30–10.45) **OL196–(LUMEX)–Nikolay Ivanov** *Application of Graphite Furnace Atomic Absorption Spectrometer with Zeeman High Frequency Polarization Modulation background correction for environmental analysis*

#### *Envir IV – Thursday 15<sup>th</sup> of June – Late Morning Session*

(11.15–11.30) **OL197–Jan Viljanen, M. A. Wakil, J. Toivonen, Z. T. Alwahabi** *Temporal Elemental Release During Biomass Combustion Using Microwave Assisted Laser-induced Breakdown Spectroscopy*

(11.30–11.45) **OL198–Zheng Wang, Q. Li, C. Huang, J. Mo, J. Ma, R. Gai** *Element Determination By Atmospheric-Pressure Solution Cathode Glow Discharge And Atomic Emission Spectrometry*

(11.45–12.00) **OL199–Giuseppe Capobianco, G. Bonifazi, V. Di Giovenale, S. Serranti** *A hierarchical classification approach for the identification of different waste polymers by hyperspectral imaging*

(12.00–12.15) **OL200–Gerrit Renner, T. C. Schmidt, M. Egelkraut–Holtus, J. Schram** *Automated Identification of Environmental Microplastics Based on FT–IR Spectroscopy*

## Fundamentals of LIBS Sessions

#### *LIBS I – Monday 12<sup>th</sup> of June – Early Morning Session*

(09.45–10.15) **IL06** Invited Lecture: **Christian G. Parigger** *Measurement of electron temperature and density in laser-induced hydrogen and laboratory air plasma*

(10.15–10.30) **OL51–Pawel Gasior, M. Kubkowska, P. Tchorz, E. Kowalska–Strzeciwlk,** *Inter-pulse delay influence on the plasma expansion dynamics in DP–LIBS investigation of a graphite sample in vacuum*

(10.30–10.45) **OL52–César Alvarez–Llomas, R. I. Á. García, J. Pisonero, N. Bordel** *Use of CaF molecular emission to improve the analytical capabilities for fluorine detection by LIBS*

#### *LIBS II – Monday 12<sup>th</sup> of June – Late Morning Session*

(11.15–11.45) **KL05–Keynote Lecture: Jörg Hermann** *Characterization of laser-produced plasmas*

(11.45–12.00) **OL54–Gianpiero Colonna, A. Laricchiuta, L. D. Pietanza** *Modeling plasma heating by fs laser pulse*

(12.00–12.15) **OL55–(IBSEN)–Thomas P. Rasmussen** *Ultra compact high resolution OEM spectrometers for LIBS*

(12.15–12.30) **OL56–Vyacheslav Lebedev** *LIBS system on the basis of Nd:YAG laser with multiloop cavity self-Q-switched by external plasma mirror*

(12.30–12.45) **OL57–Ali Safi, G. Cristoforetti, S. Legnaioli, V. Palleschi, S. H. Tavassoli, E. Tognoni** *New procedure for verification of Local Thermodynamic Equilibrium (LTE) in Laser-Induced Breakdown Spectroscopy*

#### *LIBS III – Monday 12<sup>th</sup> of June – Afternoon Session*

(14.45–15.15) **KL06–Carlos Aragón, J. A. Aguilera** *Analysis of aluminum alloys by CSigma laser-induced breakdown spectroscopy*

(15.15–15.30) **OL58–Yousfi Houssyen, A.–M. Samira, O. Ourida** *A Comparative Study of Carbon Plasma Emission in Methane and Argon Atmosphere*

(15.30–15.45) **OL59–Yoshihiro Deguchi, Z. Wang, M. Cui, Y. Fujita, R. Liu, J. Yan** *Improved Detection Ability Using Collinear Long and Short DP–LIBS*

(15.45–16.00) **OL60–Zeyad T. Alwahabi, S. J. Chen, A. Iqbal, C. Fumeaux** *Near-Field Applicators for Efficient Microwave Assisted Laser-Induced Breakdown Spectroscopy*

(16.00–16.15) **OL61–Yaser Nosrati Ghods, S. H. Tavassoli** *Effect of Laser Pulse Energy and Delay Time in Double-Pulse on laser ablation and Plasma Radiation: Modeling and Numerical Simulation*

#### *LIBS IV – Tuesday 15<sup>th</sup> of June – Early Morning Session*

(09.15–09.45) **KL13–Igor Gornushkin, A. Kazakov, R. Glaus, L. Nagli, U. Panne** *Model of Stimulated Emission in Aluminum Laser-Induced Plasma Produced by Resonance Pumping*

(09.45–10.00) **OL126–Irene Maria Carrasco–García, J. M. Vadillo, J. Laserna** *Wavelength Dependence of Surface Transformations in Femtosecond Laser Ablation of Metallic Thin-Films*

(10.00–10.15) **OL127–Thomas Dietz, M. Wolnitza, P. Kohns, G. Ankerhold** *Reactive molecular dynamic simulations to investigate molecular formation in laser-induced plasmas*

(10.15–10.30) **OL128–Ben Delaney, P. Colley, T. J. Kelly, E. T. Kennedy, J. T. Costello** *Determination of Detection Limits of Trace Elements in Aluminium Using Stagnation Layers*

(10.30–10.45) **OL129–Alexander Kramida, K. Olsen, Y. Ralchenko** *A new interactive interface to the NIST Atomic Spectra Database for LIBS spectra simulation and diagnostics*



## Geological Applications Sessions

### Geo I – Monday 12<sup>th</sup> of June – Afternoon Session

(14.45–15.15) **IL05** Invited Lecture: **Russell S. Harmon** LIBS in the Earth Sciences–Recent Applications and Current Perspectives

(15.15–15.30) **OL47**–**David R. Day** *Lithium Brine Analysis to PPM Levels using Hand Held LIBS*

(15.30–15.45) **OL48**–**Rim Alrifai**, C. Koral, M. Dell'Aglio, M. Torelli, A. De Giacomo *Non-Invasive Elemental Analysis of Gemstones by Nano Particle Enhanced Laser Induced Breakdown Spectroscopy*

(15.45–16.00) **OL49**–**Timur Akhmetzhanov, A. M. Popov, Sergey M. Zaytsev, T. A. Lavtin** *Quantification of Fe/Mn ratio in iron–manganese nodules by CF–LIBS*

(16.00–16.15) **OL50**–**Stefano Pagnotta**, S. Raneri, M. Lezzerini, M. Tamponi, B. Campanella, E. Grifoni, S. Legnaioli, G. Lorenzetti, F. Poggialini, V. Palleschi *Accuracy and precision improvement of Laser Induced Breakdown Spectroscopy (LIBS) by geostandards*

### Geo II – Tuesday 13<sup>th</sup> of June – Early Morning Session

(09.15–09.30) **OL94**–**Saara Kaski**, T. Niilahti, H. Häkkinen, S. Romppanen *Classification of sulfur minerals in vacuum ultraviolet and near-infrared spectral region* **Richard Hark**–*Analysis of Columbite–Tantalite Using Handheld LIBS*

(09.30–09.45) **OL95**–**Richard R. Hark**, M. A. Wise, R. S. Harmon, C. S. Throckmorton, A. M. Somers, L. M. Collins *Analysis of Columbite–Tantalite Using Handheld LIBS*

(09.45–10.00) **OL96**–**Giorgio Senesi**, B. Campanella, E. Grifoni, S. Legnaioli, G. Lorenzetti, S. Pagnotta, F. Poggialini, V. Palleschi, O. De Pascale *Three-dimensional compositional mapping of limestone by double-pulse micro-laser-induced breakdown*

(10.00–10.15) **OL97**–**Susanne Schröder**, K. Rammelkamp, D. Vogt, A. Cousin, O. Forni, S. Maurice, S. Clegg, R. Wiens, H. Heinz–Wilhelm *Improving Sulfur Detection in Martian Targets with time-resolved LIBS*

(10.15–10.30) **OL98**–**Simona Raneri**, G. Barone, P. Mazzoleni, M. Lezzerini, B. Campanella, E. Grifoni, Stefano Legnaioli, G. Lorenzetti, S. Pagnotta, F. Poggialini, V. Palleschi, U. Longobardo *Laser Induced Breakdown Spectroscopy (LIBS) for gemological testing: the case of corundum gems*

(10.30–10.45) **OL99**–**Russell S. Harmon**, R. R. Hark, Chandra S. Throckmorton, J. J. Gurney, A. H. Downey, A. M. Somers, L. M. Collins *Handheld LIBS as a Field Tool for Diamond Exploration–Analysis of Kimberlite Minerals*

### Geo III – Thursday 15<sup>th</sup> of June – Early Morning Session

(09.15–09.45) **IL13** Invited Lecture: **Mohamad Sabsabi**, P. Bouchard, A. Harhira, J. El Haddad, K. Rifai, F. Vanier, A. Moreau, A. Blouin *New Horizons in LIBS and Challenges for its Implementation in the Mining Industry*

(09.45–10.00) **OL183**–**Kristin Rammelkamp**, D. S. Vogt, S. Schröder, H.–W. Hübers *Investigation of Normalization Methods using Plasma Parameters for Laser Induced Breakdown Spectroscopy (LIBS) under simulated Martian Conditions*

(10.00–10.15) **OL184**–**Jens Frydenvang**, O. Forni, A. Cousin, R. C. Wiens, N. Mangold, O. Gasnault, S. Maurice and the ChemCam Team *Laser Induced Breakdown Spectroscopy (LIBS) for gemological testing: the case of corundum gems*

(10.15–10.30) **OL185**–**Mauana Schneider**, M.–D. Huang, H. Becker–Ross, B. Welz *A new approach for arsenic determination: Direct analysis of solid soil samples by HR-CS GF-AAS*

(10.30–10.45) **OL186**–**Michael I. Oshtrakh**, A. A. Maksimova, A. V. Chukin, I. Felner, G. A. Yakovlev, V. A. Semionkin *Characterization of NWA 6286 and NWA 7857 Ordinary Chondrites Using X-Ray Diffraction, Magnetization Measurements and Mössbauer Spectroscopy*

## Coal and Steel Analysis Sessions

### Tuesday 13<sup>th</sup> of June – Late Morning Session

(11.15–11.45) **IL11** Invited Lecture: **Zhe Wang**, Z. Hou, Z. Li, W. Ni, H. Yin, Y. Fu, T. Li *A set of quantification method for coal analysis using laser-induced breakdown spectroscopy*

(11.45–12.00) **OL130**–**Johannes D. Pedarnig**, S. Eschlböck–Fuchs, R. Rössler, C. M. Ahamer, L. Birklbauer, N. Huber, *Analysis of metallurgical slags in steel production by calibration-free laser-induced breakdown spectroscopy*

(12.00–12.15) **OL131**–**Guy Monfort**, G. Moréas *Strategies for the LIBS on-line analysis of transition billets in continuous casting machines*

(12.15–12.30) **OL132**–**M.C. Cui**, Y. Deguchi, Z. Z. Wang, Y. Fujita, R. W. Liu *Dynamics and Parameters of Plasma Generated by Long and Short Dual Pulses Laser Interacting with Steel Sample*

(12.30–12.45) **OL133**–**Volker Sturm**, C. Meinhardt, R. Fleige, C. Fricke–Begemann, J. Eisbach *Fast Identification of Steel Bloom Composition at a Rolling Mill by LIBS Elemental Analysis*

(12.45–13.00) **OL134**–**(SCIAPS)**–**David R. Day**, B. Connors, J. van Run *Recent Developments in Handheld LIBS and New Applications in Steel Analysis*

(13.00–13.15) **OL135**–**Nomvano Mketo**, P. N. Nomngongo, J. C. Ngila *Trace-metal Mobility in Coal Samples using Multivariate Optimised Microwave Based Sequential Extraction Method prior to Spectrometric Determination*



## LIBS imaging Session

Tuesday 13<sup>th</sup> of June – Late Morning Session

(15.00–15.30) **KL14** Keynote Lecture: **V. Motto-Ros**, F. Pelascini *Elemental imaging by LIBS: recent advances and remaining challenges*

(15.30–15.45) **OL136–(ELEMISION)–Francois Doucet** *LIBS Imaging of Drill Core Samples for the Mining Exploration*  
 (15.45–16.00) **OL137–Cassian Gottlieb**, T. Günther, S. Millar, N. Sankat, G. Wilsch *Influence of grain sizes on the quantification of LIBS measurements in concrete*

(16.00–16.15) **OL138–Violeta Lazic**, A. Palucci, M. Nuvoli, M. Pistilli, I. Menicucci, F. Colao, L. De Dominicis, S. Almaguila *Integrated Laser Sensor (ILS) for characterization and extended mapping of remote targets*

(16.15–16.30) **OL139–Morris J. J. Weimerskirch**, T. O. Nagy, A. Giesriegl, U. Pacher, W. Kautek *LIBS–Stratigraphy of protective coatings: Investigations on the wavelength dependence of the ablation rate in metals*

(16.30–16.45) **OL140–Pavel Pořízka**, J. Klus, D. Prochazka, J. Vrábel, J. Novotný, J. Kaiser *Advances in direct utilization of echellograms in LIBS analysis*

## LIBS & Raman Session

Tuesday 13<sup>th</sup> of June – Late Afternoon Session

(11.15–11.45) **KL10** Keynote Lecture: **S. Michael Angel**, P. Barnett, A. Allen *Miniature Spatial Heterodyne Spectrometers for Remote LIBS and Raman Spectroscopy*

(11.45–12.00) **OL100–(B&W TEK)–Ken Li** *NanoLIBS and its applications*

(12.00–12.15) **OL101–Sergey G. Pavlov**, J. Asemgeest, S. Schröder, U. Böttger, I. Weber, A. Greshake, H.–R. Knöfler, U. Altenberger, H. W. Hübers *Laser-ablation alteration of iron sulfides studied at different simulated planetary conditions by Raman spectroscopy*

(12.15–12.30) **OL102–Bobby Bhatt**, A. Dehayem–Massop, K. H. Angeyo *Nuclear Forensics Analysis by Combined LIBS and Raman Spectrometry*

(12.30–12.45) **OL103–(AVANTES)–Klaas Otten** *Avantes spectrometers for LIBS and Raman applications*

(12.45–13.00) **OL104–Vasily N. Lednev**, P. A. Sdvizhensky, M. Ya. Grishin, A. N. Fedorov, S. M. Pershin *Combining Raman and Laser Induced Breakdown Spectroscopy by Double Pulse Lasing*

## Industrial Application Sessions

Industrial I – Tuesday 13<sup>th</sup> of June – Early Morning Session

(09.15–09.45) **IL07** Invited Lecture: **Asmaa El hassan**, S. M. Aberkane, K. A. Elsayed, T. Kayed *A comparative study of LIBS Quantitative analysis of Al alloy using artificial neural networks and calibration methods*

(09.45–10.00) **OL62–Elise François**, O. Gazeli, S. Couris, G. Angelopoulos, A. Malfliet, B. Blanpain *Non-ferrous slag analysis using Laser-Induced Breakdown Spectroscopy (LIBS)*

(10.00–10.15) **OL63–Maurice Brogly**, D. Fischer, S. Bistac *FTIR PM–IRRAS Spectroscopy and AFM Investigations of Polymer and Copolymer Thin Films Adsorbed on Metal Substrates*

(10.15–10.30) **OL64–Sven Connemann**, C. Fricke–Begemann, R. Noll, H. Knapp, L. Horckmans, F. Bouillot, C. Gehlen, A. Ducastel, A. Stark *Automated LIBS sorting system for spent refractories from the steel industry for high-value recycling*

(10.30–10.45) **OL65–Shuzo Eto**, T. Fujii *Rapid Measurement system for concrete sample by using laser-induced breakdown spectroscopy*

Industrial II – Tuesday 13<sup>th</sup> of June – Late Morning Session

(11.15–11.45) **KL07–Sergey M. Pershin**, V. N. Lednev *Three Decades of Double-pulse LIBS: from the first steps in 1987 to modern industry applications*

(11.45–12.00) **OL66–Stanislaw Piorek** *Performance Comparison of Handheld LIBS Analyzer with that of Handheld XRF Analyzer in Composition Analysis and Grade Identification of Metallic Alloys*

(12.00–12.15) **OL67–(SHIMADZU)–Jan Knoop** *Automated contaminant analysis by FTIR microscope*

(12.15–12.30) **OL68–Sami Ul Haq**, H. Shakeel, G. Aisha, A. Nadeem *Quantitative analysis of Al–Si alloy using calibration free laser induced breakdown spectroscopy (CF–LIBS)*

(12.30–12.45) **OL69–Syedah Sadaf Zehra**, J. Costello, P. Hayden *Time resolved VUV LIBS for thin film depth profiling*

(12.45–13.00) **OL70–Héctor Morillas**, C. García–Florentino, M. Maguregui, I. Marcaida, U. Balziskuetta, J. M. Madariaga *Evaluation of deterioration processes on bricks exposed to industrial–marine environments using field and laboratory analytical methods*

(13.00–13.15) **OL71–Sebastian Breithaupt**, B. Klie, U. Giese *Surface vs. Core analysis of synthetic rubber samples and the influence on the ablation efficiency using LIBS*

*Industrial III – Tuesday 13<sup>th</sup> of June – Afternoon Session*

(15.00–15.15) OL72–Cord Fricke–Begemann, S. Connemann, F. Schreckenber, R. Noll *LIBS for identification and localization of valuable materials in electronic waste*

(15.15–15.30) OL73–(LTB)–David Mory *Recent improvements of Echelle spectrographs toward industrial applications*

(15.30–15.45) OL74–Shyama Prasad Banerjee, M. Sentis *Laser Induced Breakdown Spectroscopy for monitoring laser scribing on organic photovoltaic devices*

(15.45–16.00) OL75–Gerd Wilsh, *Laser-induced breakdown spectroscopy for the chemical investigation of concrete infrastructure*

**Biomedical Application Sessions***Biomed I – Tuesday 13<sup>th</sup> of June – Early Morning Session*

(09.15–09.45) IL08 Invited Lecture: Boris Mizaikoff *Towards IR-on-a-Chip: Is Smaller Better?*

(09.45–10.15) KL08 Invited Lecture: Paddy Hayden, M. B. Ali, S. S. Zehra *Applications of Vacuum Ultraviolet Laser Induced Breakdown Spectroscopy (VUV-LIBS) in the Analysis of Pharmaceuticals*

(10.15–10.30) OL79–Samuel Moncayo, B. Busser, M. Catinon, F. Trichard, M. S. Vincent, F. Pelascini, D. Devismes, N. Pinel, I. Tempplier, M. Vincent, V. Bonnetterre, J. Charles, L. Sancey, V. Motto-Ros *LIBS imaging for supporting medical diagnoses*

(10.30–10.45) OL80–Condon Lau, *Elemental analysis of the thyroid by laser induced breakdown spectroscopy*

*Biomed II – Tuesday 13<sup>th</sup> of June – Late Morning Session*

(11.15–11.45) KL09 Keynote Lecture: Alexander A. Kamnev, A. V. Tugarova *Microbiological Applications of Vibrational Spectroscopy: Looking inside through the Cell Wall*

(11.45–12.00) OL81–Muhammad B. Ali, P. Hayden *Vacuum Ultraviolet Laser Induced Breakdown Spectroscopy (VUV-LIBS) For Pharmaceutical Analysis*

(12.00–12.15) OL82–Paolo Armanetti, C. Avigo, A. Flori, L. Menichetti *The Photoacoustic effect in the field of biomedicine: Imaging, multi-spectral analysis in biomedical applications*

(12.15–12.30) OL83–Alessandra Gianoncelli, M. Altissimo, D. E. Bedolla, G. Kourousias *Recent achievements in Life Sciences of the TwinMic soft spectromicroscopy beamline at Elettra*

(12.30–12.45) OL84–Noureddine Cheriet, A. Boutenfouche, S. M. Aberkane, S. Abdelli-Messaci, S. Bouzid, A. Dahdouh *Discrimination of lithiasic components in kidney stones using laser induced breakdown spectroscopy*

(12.45–12.30) OL85–Zhuoyong Zhang, Q. Wu, X. Zhang, Y. Zhang, Y. Liao *Characterization of Chiral Drugs by Using Terahertz Time-Domain Spectroscopy*

*Biomed III – Tuesday 13<sup>th</sup> of June – Afternoon Session*

(15.00–15.15) OL87–Thomas Signour, L. Duponchel *Air Bio–Monitoring: a new protocol for cultureless bacteria identification by combining genomic analysis and Raman spectroscopy*

(15.15–15.30) OL88–Fiorella laquinta, C. Álvarez, P. Pizzorno, M. Pistón, A. Cousillas, N. Mañay *Determination of As, Hg, Mn and Pb in hair using atomic absorption spectrometry as biomarkers of exposure for health risk assessment*

(15.30–15.45) OL89–Viktor Kanicky, M. V. Galiova, M. Hola, T. Vaculovic *Laser ablation inductively coupled plasma mass spectrometry in elemental imaging of selected mineral and biological samples*

(15.45–16.00) OL90–Hudson Angeyo Kalambuka, D. Musyoka, A. Dehayem, K. Kaduki *Rapid Malaria Diagnostics via Peak-Free LIBS of Blood*

(16.00–16.15) OL91–Alessandra Flori, G. Giovannetti, M. F. Santarelli, V. Positano, G. D. Aquaro, L. Landini, L. Menichetti *Magnetic Resonance Chemical Shift Imaging by hyperpolarized probes: cardiac <sup>13</sup>C–spectroscopic imaging of enzymatic fluxes*

**Materials Sessions***Materials I – Tuesday 13<sup>th</sup> of June – Afternoon Session*

(15.00–15.15) OL106–Zuzana Morávková *Model of the interaction of polypyrrole with organic dyes and its influence on polypyrrole morphology – vibrational spectroscopy study*

(15.15–15.30) OL107–Eraldo Luiz Lehmann, M. A. Zezzi Arruda *Mass-charge shift ratio to increase accuracy through oxide formation of Mn, Ni and Fe focusing on their determinations by ICP-MS*

(15.30–15.45) OL108–Ana Guilherme Buzanich, A. Kulow, S. Beyer, M. Radtke, U. Reinholz, H. Riesemeier *S<sub>2</sub>XAFS: Time-resolved X-ray absorption spectroscopy in a 'single-shot' – First in situ applications*

(15.45–16.00) OL109–Tiina Virtanen, S.-P. Reinikainen, J. Lahti, M. Mänttari, M. Kallioinen *Application of principal component analysis model for real-time monitoring membrane fouling*

(16.00–16.15) OL110–Xin Zhang, L. Huang, Y. Liao, Z. Zhang *Fingerprint Identification of Inorganic Compounds Using Terahertz Time-Domain Spectroscopy*

(16.15–16.30) OL111–Ali Reza Berenji, S. F. Tayyari, M. Vakili, S. Soltani–Ghoshkhaneh *Structure, Vibrational Analysis and Intramolecular Hydrogen Bond Strength of Some 4–Amino–3–Penten–2–One Derivatives*

*Materials II – Wednesday 14<sup>th</sup> of June – Early Morning Session*

(09.15–09.30) OL141–Y.-B. Jiang, Qian Zhang, D.-D. Tao, D. Liu, N. Chen, Q. Wang, Z. Li *Innovations in Spectral Sensing Exploring Ag<sup>+</sup> Coordination Polymers Facilitated by Ag<sup>+</sup>–Ag<sup>+</sup> Interactions*

(09.30–09.45) OL142–Belgin Genc Oztoprak, E. Akman, O. Koban, M. O. Bora, A. Demir *Analysis of Laser Treated CFRP Surfaces by Laser-Induced Breakdown Spectroscopy*

(09.45–10.00) OL143–Walter Giurlani, A. Lavacchi, A. Giaccherini, F. Di Benedetto, G. Montegrossi, S. Freschi, F. D'Acapito, M. Innocenti *An innovative spectroscopic technique for the study of palladium behavior in Alkaline Fuel Cells*

(10.00–10.15) OL144–Roman J. Jedrzejczyk, P. Jodlowski, D. Chlebda, A. Dziedzicka *New sonochemically assisted synthesis of structured non-noble catalyst for methane and VOCs combustion*

(10.15–10.30) OL145–Tomasz Runka, K. Olszewska, P. Fertsch, A. Lapinski, I. Jastrzebska, R. Santillan, N. Farfán *Raman spectroscopy characterization of cyclic/acyclic molecular rotors*

**Speciation Session***Speciation Tuesday 13<sup>th</sup> of June – Afternoon Session*

(15.00–15.30) IL10 Invited Lecture: Joanna Szpunar *Spectrometric tools for selenium speciation: oxidation states, metabolites, proteins and nanoparticles*

(15.30–16.00) KL12 Keynote Lecture: Ryszard Lobinski, L. Ouerdane, *Probing for metal–ligand interactions and analysis for non-covalent metal complexes in bacteria and plants using chromatography with dual ICP MS and electrospray FT MS detection*

(16.00–16.15) OL123–Tomáš Matoušek, Z. Wang, C. Douillet, S. Musil, M. Stýblo *Direct Speciation Analysis of Arsenic in Whole Blood and Blood Plasma at Low Exposure Levels by Hydride Generation–Cryotrapping–ICP–MS: A New Trick of an Old Dog*

(16.15–16.30) OL124–Luthando Nyaba, P. N. Nomngongo *Speciation of inorganic selenium in environmental samples after suspended dispersive solid phase microextraction combined with inductively coupled plasma spectrometric determination*

(16.30–16.45) OL125–Agnieszka Nawrocka, M. Durkalec, M. Kmiecik, A. Posyniak *Speciation Analysis of Arsenic Compounds in Marine Samples*

**Atomic Spectrometry Session***Atom Spect Wednesday 14<sup>th</sup> of June – Late Morning Session*

(11.00–11.45) KL15 Keynote Lecture: Margaretha de Loos-Vollebregt, G. Grindlay, R. Serrano, J. Mora *The role of charge transfer in matrix-induced non-spectral interferences in inductively coupled plasma atomic emission and mass spectrometry*

(11.45–12.00) OL147–Daniel L. G. Borges, J. S. de Gois, T. S. de Almeida *New Findings on the Direct Analysis of Solid Samples Using Atomic and Inorganic Mass Spectrometry*

(12.00–12.15) OL148–Zhenli Zhu, C. Yang, D. He, H. Zheng *Development of a Battery-Operated, Portable Atomic Emission Analyzer for Elemental Analysis Based on Atmospheric Pressure Glow Discharge Excitation Source*

(12.15–12.30) OL149–(AGILENT)–Paolo Scardina, *Removing interferences with the MS-MS technology in triple quadrupole ICP-MS to improve the analytical detection of inorganic nanomaterials*

(12.30–12.45) OL150–Rocio Muñoz, L. Lobo, T. Kerry, C. Sharrad, R. Pereiro *Quantitative depth profile analysis of rare earth elements in corroded steel by glow discharge – time of flight mass spectrometry*

(12.45–13.00) OL151–Ilknur Durukan Temuge, Ç. A. Şahin, S. Bektaş *Ligandless Extraction of Trace Amount of Lead Ion by Solidified Floating Organic Drop Microextraction and Determination by Atomic Absorption Spectrometer*

(13.00–13.15) OL152–(ATOMTRACE)–Jakub Klus, O. Beňuš, J. Novotný, D. Prochazka, P. Pořízka, J. Kaiser *AtomAnalyzer: new dimension in spectral data analysis*

**Proteomics Session***Proteomics Wednesday 14<sup>th</sup> of June – Early Morning Session*

(09.15–09.45) IL12 Invited Lecture: Rainer Bischoff, T. Zhang, F. T. G. van den Brink, M. Odijk, H. P. Permentier *Electrochemical, site-specific peptide bond cleavage as a novel approach in protein analysis*

(09.45–10.15) KL16 Keynote Lecture: Qiuquan Wang, Y. Liang, C. Liu, N. Tang, L. Yang *Metal-Tagging Strategy for Bioanalysis: Quantification of Protein Biomarkers and Counting Cells*

(10.15–10.30) OL153–Rosario Pereiro, M. C. Alonso, B. Fernández, H. Traub, L. Álvarez, H. G. Igle-sias, N. Jakubowski *Bioimaging of proteins in biological tissue sections by LA-ICP-MS using bioconjugated gold nanoclusters*

(10.30–10.45) OL154–Sara Rodríguez-Menéndez, H. González, B. Fernández, M. García, L. Álvarez, M. Coca-Prados, R. Pereiro *Comprehensive quantitative study of Zn and Metallothioneins in eye tissue sections and cultured cells by mass spectrometry-based methodologies*

## Fuels Session

*Fuels Wednesday 14<sup>th</sup> of June – Early Morning Session*

(09.15–09.45) **KL20** Keynote Lecture: **Érico Marlon de Moraes Flores** *Feasible Sample Preparation Methods for further Rare Earth Elements Determination*

(09.45–10.00) **OL163**–Przemysław Jodłowski, R. J. Jędrzejczyk, D. Chlebda, M. Gierada, J. Łojewska *In situ spectroscopic studies of methane catalytic combustion over Co, Ce and Pd mixed oxides deposited on a steel surface.*

(10.00–10.15) **OL164**–Carlos Sánchez-Rodríguez, C.–P. Lienemann, F. Vanhaecke, J.–L. Todolí *Determination of metals and metalloids in bioethanol samples using a total sample consumption system coupled to ICP techniques*

(10.15–10.30) **OL165**–Zofia Kowalewska, Ł. Gościński, J. Pilarczyk *Feasibility of high resolution continuum source flame molecular absorption spectrometry for Si determination in organic solutions via SiO molecule absorption*

## Liquid Analysis Session

*Liq. Analysis Wednesday 14<sup>th</sup> of June – Early Morning Session*

(09.15–09.45) **KL22** Keynote Lecture: **Montserrat Hidalgo** *Analysis of liquid samples: a great challenge for LIBS*

(09.45–10.00) **OL173**–Mayo Villagrán–Muniz, O. G. Miranda, T. García–Fernández, F. Bredice, C. Sánchez–Aké *Study of laser ablation of water droplets with gold nanoparticles*

(10.00–10.15) **OL174**–Şerife Yalçın, N. Aras, *Investigating silicon wafer based substrates for ultra–trace determination of metal solutions: Dry droplet analysis by LIBS*

(10.15–10.30) **OL175**–Francisco Ruiz, L. Ripoll, M. Hidalgo, A. Canals *Solid phase microextraction (SPME) using carbon–based screen–printed electrodes combined with LIBS technique detection for sensitive elemental analysis*

(10.30–10.45) **OL176**–Laura Ripoll, F. Ruiz, A. M. Hidalgo, A. Canals, S. Legnaioli, V. Palleschi *Evaluating the use of Thin Film Microextraction (TFME) with laser–induced breakdown spectroscopy (LIBS) for the detection of trace metals in liquid samples*

## Forensic Application Session

*Forensic Wednesday 14<sup>th</sup> of June – Late Morning Session*

(11.00–11.45) **KL17** Keynote Lecture: **Jun Kawai** *Fabrication and Falsification in XRF, ICP–AES, HG–AAS and GC–MS in Forensic Analyses in Japan*

(11.45–12.15) **KL18** Keynote Lecture: **Luigia Sabbatini**, G. Germinario, S. Garrappa, I. D. van der Werf, A. Mirabile *An integrated multi analytical approach for the investigation of modern inks*

(12.15–12.45) **KL19** Keynote Lecture: **Israel Schechter** *Detection and Mapping of Trace Materials on Surfaces Under Ambient Conditions using Multiphoton Electron Extraction Spectroscopy (MEES) and Comparison to Traditional Spectroscopies*

(12.45–13.00) **OL155**–Jun–Ho Yang, J. J. Yoh *Separation of Overlapping Latent Fingerprint using Laser–Induced Breakdown Spectroscopy Combined with Multivariate Analysis*

(13.00–13.15) **OL156**–Marek Kotrlý, R. Šefců *Analysis techniques for multicomponent samples in forensic fields*

## Vapor Generation & Sample Introduction Techniques Session

*Vapor Generation Wednesday 14<sup>th</sup> of June – Late Morning Session*

(11.15–11.45) **KL21** Keynote Lecture: **Jiří Dědina**, J. Kratzer, A. Obrušník, M. Talába, P. D. Hydride Atomizers for Atomic Absorption and Atomic Fluorescence Spectrometry – New Horizons

(11.45–12.00) **OL167**–Enea Pagliano, *Recent developments in the determination of inorganic anions by gas chromatography mass spectrometry*

(12.00–12.15) **OL168**–Jan Kratzer, S. Musil, M. Svoboda, J. Dědina *Dielectric Barrier Discharge Atomizers of Volatile Species for Atomic Spectrometry: Applications and Mechanisms*

(12.15–12.30) **OL169**–Karel Marschner, S. Musil, J. Dědina *Cleavage of As–C Bond during Chemical Hydride Generation*

(12.30–12.45) **OL170**–Jürgen Schram, J. Schlag, S. Reichenberger, G. Marzun, S. Barcikowski *Pulsed Laser Ablation in Liquids as Digestion Method for Inductively Coupled Plasma Optical Emission Spectroscopy*

(12.45–13.00) **OL171**–Kazuaki Wagatsuma, Y. Toya, T. Itagaki *Correlation between Gas Temperature and Atomization Behavior of Analyte Elements in Flame Atomic Absorption Spectrometry Estimated with a Multi–Wavelength High–resolution Spectrometer*

## Chemometrics Session

*Chemometrics Wednesday 14<sup>th</sup> of June – Late Morning Session*

(11.00–11.45) **KL23** Keynote Lecture: **Jean–Baptiste Sirven**, M. El Rakwe *Experimental designs in LIBS*

(11.45–12.00) **OL177**–Praveen Devangad, V. K. Unnikrishnan, M. Yogesha, M. M. Tamboli, K. M. Muhammed Shameem and C. Santhosh *Support vector machines for the classification and quantification of borosilicate glass samples using Laser Induced Breakdown Spectroscopy (LIBS)*



- (12.00–12.15) **OL178–Euseok Hwang**, H. Jang, S. Shin, S. Jeong *Likelihood based Compressive Spectrum Processing for Classification of Same-base Alloys by Laser-induced Breakdown Spectroscopy*
- (12.15–12.30) **OL179–Onkangi Nyairo Joshua**, M. David, K. H. Angeyo *Utility of Machine-Learning Enabled LIBS in Forensic Analysis of High Level Nuclear Waste*
- (12.30–12.45) **OL180–Daniel Diaz**, D. W. Hahn, A. Molina *Application of Conditional Analysis to the Quantification of Au in Ores by Laser-Induced Breakdown Spectroscopy*

## Clinical and Pharma Sessions

### Pharma I – Thursday 15<sup>th</sup> of June – Early Morning Session

- (09.15–09.45) **IL19** Invited Lecture: **Rosalba Gaudiuso**, N. Melikechi, E. Ewusi-Annan *Cancer Diagnosis using LIBS and Machine Learning Tools: Progress and Challenges*
- (09.45–10.00) **OL205–Yong Liang**, L. Yang, Q. Wang *ICPMS-Based Quantitative Analysis of Glyco-PTMs via Metabolism-Mediated and Clickable Lanthanide-Tagging Strategy*
- (10.00–10.15) **OL206–Francesca G. Bellagambi**, T. Lomonaco, S. Ghimenti, V. Barletta, A. D'Agostino, D. Biagini, M. Marzilli, M. G. Trivella, F. Di Francesco, R. Fuoco *Determination of biomarkers in oral fluid for monitoring heart failure patients*
- (10.15–10.30) **OL207–Marcia F. Mesko**, V. C. Costa, D. La Rosa Novo, R. Mendes Pereira, L. S. Fagundes Pereira, R. Sogari Picoloto, *Determination of Cd and Pb in Creamy, Opaque and Shimmering Lipstick by ICP-MS*

### Pharma II – Thursday 15<sup>th</sup> of June – Late Morning Session

- (11.15–11.30) **OL209–Joanna Chwiej**, M. Palczynska, A. Skoczen, K. Janeczko, C. Sandt, R. Simon, Z. Setkowicz *The use of X-ray fluorescence and FTIR microspectroscopy for the highly spatially resolved analysis of elemental and biochemical changes occurring in the hippocampal formation during postnatal brain development*
- (11.30–11.45) **OL210–Irina V. Alenkina**, A. Kumar, A. L. Berkovsky, M. I. Oshtrakh *Comparative Analysis of the Heme Iron Electronic Structure and Stereochemistry in Tetrameric Rabbit Hemoglobin and Monomeric Soybean Leghemoglobin a Using Mössbauer Spectroscopy with a High Velocity Resolution*
- (11.45–12.00) **OL211–Gul Sirin Ustabasi**, S. Akman, A. Baysal *Distribution of trace elements in tobacco and shisha products in Turkey and accumulation on their smoke*

### Pharma III – Thursday 15<sup>th</sup> of June – Afternoon Session

- (14.15–14.45) **KL27** Keynote Lecture: **Fabio Di Francesco**, B. Melai, N. Calisi, A. Kirchhain, F. Vivaldi, R. Fuoco, P. Salvo *Flexible and disposable sensors based on graphenic materials for wound monitoring*
- (14.45–15.00) **OL214–Sofia Pessanha**, J. Silveira, F. Chasqueira, J. Godinho, A. Mata, M. L. Carvalho *Non-destructive spectroscopic techniques applied to dentistry re-search*
- (15.00–15.15) **OL215–Tommaso Lomonaco**, S. Ghimenti, F. G. Bellagambi, D. Biagini, V. Barletta, A. D'Agostino, D. Morrone, M. Marzilli, M. G. Trivella, F. Di Francesco, R. Fuoco *Determination of volatile organic compounds in human breath for monitoring heart failure patients*
- (15.15–15.30) **OL216–Sungho Jeong**, Y. Moon, J. H. Han, J.-H. Choi *Detection and Mapping of Cutaneous Melanoma Using Laser Induced Breakdown Spectroscopy*
- (15.30–15.45) **OL217–Sanja Živković**, M. Momcilovic, J. Savovic *Application of TEA CO<sub>2</sub> LIBS for Elemental Analysis of Powdered Biological Samples*
- (15.45–16.00) **OL218–Natalia Miliszkiewicz**, S. Walas, A. Tobiasz, E. Grygo-Szymanko, D. Dudek-Adamska *Comparison of selected calibration approaches in LA-ICP-MS studies of Mg and Zn distribution in rat brain tissue*

## Underwater LIBS Session

### Underwater LIBS Thursday 15<sup>th</sup> of June – Early Morning Session

- (09.15–09.45) **KL28** Keynote Lecture: **Tetsuo Sakka**, A. Kawasaki, T. Honda, A. Matsumoto, K. Amano, N. Nishi *Chemical reactions in the plasma for quantitative underwater LIBS*
- (09.45–10.00) **OL221–Blair Thornton**, T. Takahashi, T. Sakka *Reflections on 5 years of LIBS Deployments for Deep-Sea Research*
- (10.00–10.15) **OL222–Soichi Yoshino**, T. Takahashi, B. Thornton *Analysis of underwater long-Pulse LIBS signals using Artificial Neural Networks*
- (10.15–10.30) **OL223–Marcella Dell'Aglio**, M. López-Claros, G. Valenza, A. Santagata, A. De Giacomo, F. J. Fortes, J. J. Laserna *Single and Double pulse laser-induced breakdown spectroscopy of solids in water: effect of hydrostatic pressure on laser induced plasma, cavitation bubble and emission spectra*
- (10.30–10.45) **OL224–Tomoko Takahashi**, B. Thornton, Y. Takaya, T. Nozaki, T. Sato, T. Ohki, E. K. Ohki, T. Sakka *Quantitative elemental analysis of water-submerged solids using PLS with temperature segmented database for LIBS*

## Fundamentals of Mass Spectrometry Session

Mass Spect Thursday 15<sup>th</sup> of June – Late Morning Session

(11.15–11.45) IL14 Invited Lecture: **Maria Careri** *Advances and future trends in desorption electrospray-mass spectrometry*

(11.45–12.15) KL24 Keynote Lecture: **Ewa Bulska**, A. Konopka, A. Łuciuk, A. Krata, A. Ruszczyńska, B. Wagner, M. Wojciechowski *Certified Reference Materials for Atomic and Molecular Mass Spectrometry*

(12.15–12.30) OL187–(PERKIN ELMER)–**Chady Stephan**, R. Magarini, M. Buonaguidi *Trends in Single Particle and Single Cell ICP-MS Analysis - Significant Instrument Settings and their Implications on Data Quality*

## Nano-LIBS Session

NanoLibs Thursday 15<sup>th</sup> of June – Afternoon Session

(14.15–14.45) KL29 Keynote Lecture: **Alessandro De Giacomo**, C. Koral, R. Alrifai, G. Valenza, R. Gaudioso, M. Dell'Aglio, *Perspectives of Nanoparticle Enhanced Laser Induced Breakdown: the laser matter interaction under NPs control*

(14.45–15.15) IL20 Invited Lecture: **Citlali Sánchez-Aké**, T. García-Fernández, M. Villagrán-Muniz, F. Bredice, B. de la Mora, J. L. Benítez, R. Castañeda-Guzmán *Laser-induced nanoparticle formation and its application for LIBS enhancement*

(15.15–15.30) OL225–**Alexandre Semerok**, S. V. Fomichev *Nano-sampling of metals with ultra-short laser pulses*

(15.30–15.45) OL226–**Francesco Poggialini**, B. Campanella, E. Grifoni, S. Legnaioli, G. Lorenzetti, S. Pagnotta, V. Palleschi *Green Synthesis of Silver Nanoparticles and Their Application in the Laser Induced Breakdown Spectroscopy Technique*

(15.45–16.00) OL227–**Ashraf M. EL Sherbini**, F. H. Alkallas, C. G. Parigger *On nanoparticle enhanced laser-induced emission spectroscopy*

(16.00–16.15) OL228–**Kemal Efe Eseller**, M. S. Topcu, A. Ceylan, B. Sezer, G. Bilge, I. H. Boyacı *Development of a New Method for Structural Analysis Of Ge Nano-particles Embedded ZnO Thin Films By Laser Induced Breakdown Spectroscopy*

(16.15–16.30) OL229–**Pablo Purohit Pacheco** *Attogram sensitivity through laser-induced breakdown spectroscopy of single optically-trapped nanoparticles*

## Computational Spectroscopy Session

CompChem Thursday 15<sup>th</sup> of June – Afternoon Session

(14.15–14.45) IL15 Invited Lecture: **Vincenzo Barone** *The Virtual Multifrequency Spectrometer: status and perspectives of an undergoing project*

(14.45–15.15) IL16 Invited Lecture: **Stanislav Zálíš**, M. Pižl, A. Vlček Jr. *Quantum Chemical Interpretation of Spectral Properties of Organometallic Complexes in Ground, Excited and Different Redox States.*

(15.15–15.30) OL188–**Alberto Baiardi**, J. Bloino, Vincenzo Barone *Accessible accurate simulation of vibrational and electronic spectra of medium-to-large molecular systems: the virtual spectrometer*

(15.30–15.45) OL189–**Lorenzo Pardini**, S. Löffler, G. Biddau, R. Hambach, U. Kaiser, C. Draxl, P. Schattschneider *Mapping Atomic Orbitals with the Transmission Electron Microscope: Images of Defective Graphene Predicted from First-Principles Theory*

(15.45–16.00) OL190–**Laura Zanetti-Polzi**, I. Daidone, A. Amadei *Modeling amide I infrared spectra of proteins: insights from a perturbative approach*

(16.00–16.15) OL191–**Mauro Guerra**, J. M. Sampaio, F. Parente, J. P. Marques, P. Indelicato, J. P. Santos *High accuracy simulation of XRF spectra of transition metals*

(16.15–16.30) OL192–**Marco Fusè**, A. Baiardi, V. Barone, J. Bloino *Computational modelling of chiroptical properties of transition metal complexes*

## Nuclear Applications Session

NuclearApp Thursday 15<sup>th</sup> of June – Afternoon Session

(14.15–14.45) IL17 Invited Lecture: **Madhavi Martin**, B. Bennett, E. Garlea *Evaluation of corrosion on materials at the Y-12 Nuclear Security Complex using Hand-Held Laser-Induced Breakdown Spectroscopy*

(14.45–15.15) IL18 Invited Lecture: **Roger C. Martin**, M. Z. Martin, J. H. Miller *Twenty Years of LIBS at Oak Ridge National Laboratory: Nuclear Applications and Future Promise*

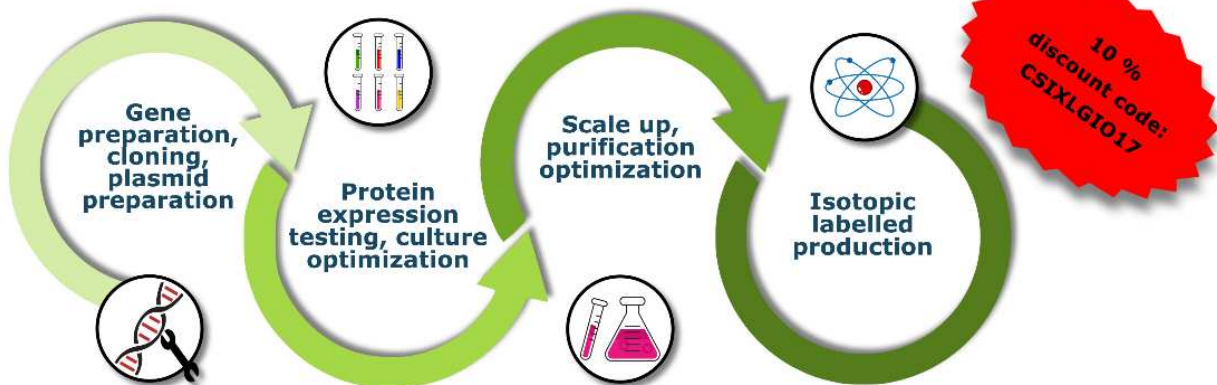
(15.15–15.45) KL26–**Francesco Colao**, S. Almaviva, L. Caneve, R. Fantoni, V. Lazic, G. Maddaluno, A. Palucci *Development of a LIBS system for applications in Frascati tokamak upgrade*

(15.45–16.00) OL202–**Kristian Myhre** *Analysis of Separation Processes for the Production of Radioisotopes Using Laser-Induced Breakdown Spectroscopy*

(16.00–16.15) OL203–**Juma Moses Wabwile**, K. H. Angeyo, A. Dehayem-Massop *Quantitative Raman Microspectrometry of Ur*

(16.15–16.30) OL204–**Pavel Veis**, M. Anguš, J. Miškovičová, M. Suchoňová *Simultaneous echelle broadband and high resolution OES study for CF LIBS analysis of W-based materials in thermonuclear fusion*

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## Poster Sessions I

Monday 12<sup>th</sup> of June 17:00-18:30

**PP1 Muhammad Alli** *Vacuum Ultraviolet Laser Induced Breakdown Spectroscopy (VUV-LIBS) For Pharmaceutical Analysis* M. Alli, P. Hayden

**PP2 Andrea Antunes** *Analysis of the roles of trace elements in malignant breast tumor in canine patients using Energy Dispersive X-ray Fluorescence (EDXRF) Technique* S.S. Sakamoto, A.L. Andrade, M.C.R. Luvizotto, Ferreira G.T.N.M., M. Scapin, A. Antunes

**PP3 Andrea Antunes** *Monitoring the incorporation of hydroxyapatite on chitosan scaf-folds using LIBS* A. Antunes, J. S. Cabral, B. Sakamoto, G. Nicolodelli, D. M. B. P.C. Milori, M. F. Raposo

**PP4 Pedro Barrulas** *Local Production or Imported Gods? Multi-analytical Investigations of Archaeological Glazed Ceramics (XVIth-XVIIIth centuries) from Largo do Jesus, Lisbon* P. Barrulas, M. Beltrame, G. Cardoso, A.F. Maurer, J. Mirão, A. Candeias

**PP5 Rainer Bischoff** *Bioconjugated supramolecular exo-functionalized palladium cages to peptides for biomedical applications* J. Han, A. Schmidt, H. P. Permentier, R. Bischoff, P. Horvatovich, A. Casini

**PP6 Rainer Bischoff** *Catalytic N-dealkylation of Drug Molecules on a Nanoporous Gold Surface* T. Yuan, J. Wu, T. Zhang, P. Rudolf, R. Bischoff, H. Permentier

**PP7 Carlo Bottaini** *Chemical characterization of a collection of metallic oil lamps from Gharb al-Andalus (Southern Portugal): An in-situ and non destructive approach by handheld X-Ray Fluorescence spectrometer and open source Monte Carlo simulation code*, C. Bottaini, A. Brunetti, J. Mirão, H. Catarino, A. Candeias, R. J. Silva

**PP8 Antonio Brunetti** *Nuragic votive swords from Sardinia (Italy): assessing alloy's composition by EDXRF/Monte Carlo Simulations*, A. Brunetti, A. Depalmas, N. Schiavon

**PP9 Beatrice Campanella** *Chemical methodologies for proteins analysis. A focus on conformational studies based on Fourier Transform Infrared Spectroscopy* E. Bramanti, B. Campanella

**PP10 Maria-Luiza Carvalho** *Two paintings, similar gold leaf manufacturing? Nondestructive determination of gold leaf thickness in panel paintings* V. Antunes, V. Serrão, A. Candeias, J. Mirão, M. L. Carvalho, S. Pessanha, N. Fernandes, M. Manso

**PP11 Adolfo Cobo** *Automatic classification of metal alloys from their LIBS spectra and its robustness against spectrometer decalibration* A. Cobo, A. Picón, M. Martínez, C. López-Sarachaga, Z. Amondarain, J. Miguel López-Higuera

**PP12 Ioana Maria Cortea** *Degradation assessment of parchment manuscript at macro- and molecular level using an non-invasive approach* I. M. Cortea, L. Ghervase, R. Rădvan, L. Ratoiu

**PP13 Mafalda Costa** *Multi-analytical approach to the study of the European glass beads found in the tombs of the Church of Kulumbimbi (Angola)* M. Costa, P. Barrulas, M. da Conceição Lopes, J. Barreira, B. Clist, K. Karklins, K. Bostoen, M. da Piedade de Jesus, S. da Silva Domingos, L. Moens, P. Vandenabeele, J. Mirão

**PP14 Damien Devismes** *Bayesian Naïve Classification for LIBS* D. Devismes, F. Pelascini

**PP15 Gianni Gallelo** *The source of the building stones from the Sagunto Castle archaeological area and its surroundings* G. Gallelo, M. Ramacciotti, M. Lezzerini, E. Hernandez, M. Calvo, A. Morales, A. Pastor, M. De la Guardia

**PP16 Esperanza Garcia-Ruiz** *Use of CaCl for the direct determination of Cl by high-resolution Continuum source graphite furnace molecular absorption spectrometry* E. García-Ruiz, A. Guarda, I. Andrés, M. Aramendía, P. C. do Nascimento, M. Resano

**PP17 Alessandra Gianoncelli** *Nano-imaging of environmental dust in human lung tissue by Soft X-ray and hard XRF Microscopy* A. Gianoncelli, C. Rizzardi, D. Salomon, V. Canzonieri, L. Pascolo

**PP18 María González Cabrera** *Raman spectroscopy for the characterization of a polychromed marble decorative revetment from the Alhambra* M. González Cabrera, P.A. Arjonilla, M.J. de la Torre López, E. Correa Gómez, R. Rubio Domene, A.A. Domínguez-Vidal, M.J. Ayora-Cañada

**PP19 Candace Harris** *Partial Least Squares Calibration models toward the determination of the LOD in <sup>90</sup>Zr and <sup>94</sup>Zr generated by zirconium metallic particles on silica substrates via Laser Ablation Molecular Isotopic Spectroscopy (LAMIS)* C.D. Harris, C. Akpovo, L. E. Johnson, A. C. Stowe

**PP20 Niklas Hausmann** *Archaeological and Climatic data from elemental ratios using rapid analysis of shell carbonate with LIBS* N. Hausmann, P. Siozos, D. Anglos

**PP21 Alexander A. Kamnev** *Methodological Effects in FTIR Spectroscopy: Implications for Structural Analyses of Biopolymers* A. A. Kamnev, Y. A. Dyatlova, A. V. Tugarova

**PP22 Albert Kéri** *LA-ICP-MS examination of mummy hair strands from the archeological artifacts found in the Dominican Church in Vác, Hungary* J. Balázs, G. Pálfi, I. Szikossy, Á. Braun, A. Kéri, G. Galbács

**PP23 Rezida Khramchenkova** *Research of Islamic Enamel Glass from Excavations at Bolgar Settlement (Russia)* R. Khramchenkova, A. Gubaidullin, R. Sharifullin, E. Nujdin

**PP24 Jakub Klus** *Evaluation of ensemble classification methods in laser-induced breakdown spectroscopy measurements* J. Klus, P. Pořízka, D. Prochazka, J. Novotný, K. Novotný, A. Hrdlička, J. Kaiser

**PP25 George Kourousias** *Simulation of Artefacts in X-ray Florescence Microscopy Based on Sample Topography* F. Billè, G. Kourousias, A. Gianoncelli

**PP26 Violeta Lazić** *Characterization of pigment compositions by LIBS beyond limits of XRF and PIXE techniques* V. Lazić, R. Fantoni, M. Vadrucchi



- PP27 Roberta G. Leitão** *Multielemental mapping by scanning synchrotron x-ray fluorescence in tumor human cells prostatic supplemented with zinc* K. M. J. Rocha, R. G. Leitão, E. G. Oliveira Barros, M. Aparecida Oliveira, C. G. L. Canellas, M. J. Anjos, L. E. Nasciutti, R. T. Lopes
- PP28 Roberta G. Leitão** *Study of elemental distribution in human prostatic carcinoma cell spheroid culture using synchrotron radiation based x-ray fluorescence* K. M. J. Rocha, R. G. Leitão, E. G. Oliveira-Barros, M. Aparecida Oliveira, C. G. L. Canellas, M. J. Anjos, L. E. Nasciutti, R. T. Lopes
- PP29 Yong Liang** *Biospecific Metabolism Based and Click Chemistry Mediated Euro-pium Tagging Enable the Determination of D-Alanine Density of Bacterial Cell Wall Peptidoglycan Layers Using ICP-MS* Y. Liang, Q. Wang
- PP30 Tommaso Lomonaco** *On-sorbent derivatization of carbonyl compounds in exhaled breath* T. Lomonaco, A. Romani, S. Ghimentì, M. Onor, D. Biagini, F. G. Bellagambi, F. Di Francesco, R. Fuoco
- PP31 Katarzyna Łuczyńska** *Structure-Spectra Correlations in Anilate Complexes with Picolines* K. Łuczyńska, K. Drużbicki, K. Lyczko, Jan. Cz. Dobrowolski
- PP32 Raquel C. Machado** *Determination of As in complex samples using solid sampling high-resolution continuum source graphite furnace atomic absorption spectroscopy* R. C. Machado, M. Aramendia, Ana Rita A. Nogueira, M. Resano
- PP33 Ana Manhita** *On the possibilities of Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) for the determination of heavy metal contamination of osteological remains and ceramics - an archaeometric study* A. Manhita, P. Barrulas, M. da Conceição Lopes, F. Vanhaecke, C. Barrocas Dias
- PP34 Marta Manso** *In situ analysis of paper documents using portable EDXRF setup with triaxial geometry* S. Pessanha, J. M. Sampaio, M. Luisa Carvalho, M. Manso
- PP35 Marta Manso** *Multi-analytical study of foxing stains on paper* M. Nunes, C. Relvas, M. Manso, M. L. Carvalho, P. Barrulas, C. Miguel, A.T. Caldeira, F. Figueira, T. Ferreira
- PP36 Konstantinos Marmatakis** *LIBS-SSI-MS: Simultaneous elemental and molecular analysis of metal containing biomolecules* K. Marmatakis, S. A. Pergantis, D. Anglos
- PP37 Maripaz Mateo** *Laser Induced Breakdown Spectroscopy applied to the evaluation of nanoparticles treatments on limestones* M. Mateo, J. Becerra, A.P. Zaderenko, P. Ortiz, G. Nicolas
- PP38 Maripaz Mateo** *Laser-induced breakdown spectroscopy analysis of Titanium-Niobium coatings generated by laser cladding for its potential use in orthopedic implants* M. Mateo, J. M. Amado, M. J. Tobar, A. Yañez, G. Nicolas
- PP39 Takeshi Minami** *Effect of Gypsum on Sulfur Isotope Ratio of Vermilion Painted on Gypsum Wall* T. Minami, E. Tsantini, K. Takahashi
- PP40 Massimo Onor** *Potentiometric Biosensor for Non-invasive Lactate Determination in Human Sweat* M. Onor, S. Gufoni, T. Lomonaco, S. Ghimentì, F. Sorrentino, E. Bramanti
- PP41 Iacopo Osticioli** *New insights into understanding the optical properties of lead-based white pigments* D. Ciofini, I. Osticioli, A.A. Mencaglia, S. Siano
- PP42 Lorenzo Pardini** *The NOMAD (Novel Materials Discovery) Laboratory* L. Pardini, C. Draxl, M. Scheffler
- PP43 Mariela Pistón** *LIBS applied to the study of metal archaeological pieces of museum collections in Uruguay* L. Beovide, M. Knochen, M. Pistón
- PP44 Eva Pospíšilová** *Laser-Induced Breakdown Spectroscopy for depth-profile analysis of historical painting model samples* E. Pospíšilová, K. Novotný, J. Kaiser, P. Pořízka, R. Ševčík, D. Hradil, J. Hradilová
- PP45 Lucilla Pronti** *Characterisation of commercial alizarin-based lakes by means of spectroscopic techniques* L. Pronti, J-B. Mazzitelli, M. P. Bracciale, L. Massini Rosati, A. Candida Felici, C. Vieillescazes, M. L. Santarelli
- PP46 Ignasi Queralt** *Total reflection X-ray fluorescence spectrometry as fast analytical technique for human placenta sample analysis* E. Margu, P. Ricketts, H. Fletcher, A. G. Karydas, A. Migliori, J.J. Leani, M. Hidalgo, Ignasi Queralt, M. Voutchkov
- PP47 Simona Raneri** *Decorative stones characterization through spectroscopic methods: mosaic tesserae from an outstanding late Roman villa in Tuscany* S. Raneri, F. Cantini, V. Palleschi, S. Legnaioli, S. Pagnotta, G. Lorenzetti, M. Lezzerini
- PP48 Simona Raneri** *Mural painting in Tuscany during the Middle Age: a spectroscopic investigation on pigments and painting technique* M. Lezzerini, F. Cantini, Simona Raneri, R. Belcari, S. Pagnotta, G. Lorenzetti, S. Legnaioli, V. Palleschi
- PP49 Elena Salernitano** *Demonstration of eco friendly tanning cycle by spectroscopic techniques (LIFE14 ENV/IT/000443 LIFETAN)* A. Dall'Ara, E. Bramanti, M. Roig, M. Sabatini, M. Cobo, E. Salernitano, F. Bezzi
- PP50 Elena Salernitano** *Eco friendly leather: Energy Dispersive X-Ray Spectroscopy combined with Scanning Electron Microscopy and Thermogravimetric Analysis (LIFE14 ENV/IT/000443 LIFETAN)* E. Salernitano, A. Dall'Ara, A. Strafella, E. Bramanti
- PP51 Roberto Sangines** *Development of a fitting algorithm for spectral analysis in a Laser Induced Breakdown Spectroscopy system* R. Sanginés, W. Lee, A. Preciado-Grijalva, O. Hernández-Utrera, N. Abun-diz-Cisneros, R. Machorro-Mejía
- PP52 Ana Beatriz Santos da Silva** *Direct determination of TiO<sub>2</sub> as Ti used as digestibility marker in bovine faeces by Laser-Induced Breakdown Spectroscopy (LIBS)* A. B. Santos da Silva, E. R. Pereira-Filho, A. R. de Araujo Nogueira
- PP53 Danielle Santos de Almeida** *Iron, Copper and Zinc mapping analysis of Swiss mice brains on experimental model of Alzheimer's disease induced by  $\beta$ -amyloid oligomers* D. S. de Almeida, M. de Melo Brígido, M. José dos Anjos, S. Teixeira Ferreira, A. Santos de Souza, R. Tadeu Lopes

- PP54 Radka Šefců** *A multi-technique approach for determining the provenance of the mineral fluorite used as an artistic pigment* R. Šefců, J. Mizera, D. Koloušek
- PP55 Radka Šefců** *The characterization of materials from the Norbert Grund's paint-ings on metal plate support* R. Šefců, M. Vondráčková, T. Trojek, V. Pitthard
- PP56 Eugenia Shaykhutdinova** *Comparative analysis of casting technologies used for the manufac-turing of cast iron dishware in the towns of Volga Bolgaria in 13th-15th centuries (Tatarstan, Russia)* E. Shaykhutdinova, R. Khranchenkova, A. Belyaev, A. Sitdikov, R. Yanbaev
- PP57 Pavlína Škarková** *Comparative investigation of toxicity bioaccumulation and distribution of Cd-based Quantum dots and Cd salt in freshwater plant Lemna minor* P. Škarková, K.I Novotný, P. Pořízka, J. Klus, P. Luba, J. Kaiser
- PP58 Simon Steger** *Non-invasive spectroscopic study on a modern reverse glass paint-ing: Marianne Uhlenhuth's "Ohne Titel, 1954"* S. Steger, O. Hahn, I. Rabin, H. Stege
- PP59 Imre Szalóki** *X-ray fluorescence microanalysis of cucumber hypocotyls using synchrotron radiation* I. Szalóki, G. Radócz, A. Gerényi
- PP60 Estrella Teran Hinojosa** *Charazeterization of fibrotic liver tissue by LIBS* E. Teran-Hinojosa, H. Sobral
- PP61 Csilla Noémi Tóth** *The elemental concentration of blood serum of patients with autoimmune diseases determined by MP-AES method* C. N. Tóth, E. Baranyai, I. Csípő, T. Tarr, M. Zeher
- PP62 Anna Tugarova** *FTIR and Raman Spectroscopic Studies of Selenium Nanoparticles Synthesised by the bacterium Azospirillum thiophilum* A. V. Tugarova, P. V. Mamchenkova, Yu. A. Dyatlova, A. A. Kamnev
- PP63 Qian Wang** *Characterization of the Aggregation Mechanism of Amyloid- $\beta$  peptides with Cu<sup>2+</sup>/Zn<sup>2+</sup> Using Fluorescence Correlation Spectroscopy* Q. Wang, Yun-Bao Jiang

## Poster Sessions II

Tuesday 13<sup>th</sup> of June 17:30-19:00

**PP1 Pavlína Škarková** *Study of selectivity of Nanoparticle Enhanced Laser-Induced Breakdown Spectroscopy signal enhancement* L. Sládková, P. Pořízka, J. Klus, P. Škarková, B. D. Prochazka, M. Remešová, K. Novotný, L. Čelko, J. Kaiser

**PP2 Juri Agresti** *Control of the depth resolution and crater diameter in elemental depth profiling based on laser ablation* J. Agresti, S. Siano

**PP3 Christoph Ahamer** *On the emission enhancement in dual-pulse femtosecond laser-induced breakdown spectroscopy of metals* C. M. Ahamer, K. M. Riepl, N. Huber, J. D. Pedarnig

**PP4 Vanessa Nunes Alves** *Chromium speciation using Magnetic magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles synthesized by coprecipitation method and detection by FAAS* V. Nunes Alves, C. A. de S. Silva

**PP5 Alena V. Amosova** *Application of WDXRF analysis for paleoclimatic investigations* A. Amosova, V. Chubarov

**PP6 Alena V. Amosova** *Geochemical characteristic of bottom sediments using X-ray fluorescence spectra* A. Amosova, V. Chubarov

**PP7 Francisco Ardini** *Antarctic Environmental Specimen Bank: A playground for analytical spectroscopists* F. Ardini, A. Bazzano, F. Soggia, M. Grotti

**PP8 Asu Ece Atespare** *Determination of Various Minerals in Rice Samples Sold in Turkey using microwave induced plasma optical emission spectrometry* E. Atespare, N. Ozbek, H. Tinas, S. Akman

**PP9 Dilek Bakircioglu** *Simultaneous Determination of Copper, Iron, Chromium, Lead, Manganese, Magnesium, Nickel and Sodium in Chocolate Samples by Flame Atomic Absorption Spectrometry After Extraction Induced by Emulsion Breaking* D. Bakircioglu, N. Topraksever, A. Gogercin, Y. Bakircioglu Kurtulus

**PP10 Yasemin Bakircioglu Kurtulus** *A Novel, Rapid and Simple Extraction Induced by Emulsion Breaking Procedure for Cu, Mn and Ni Determination in Margarine* Y. Bakircioglu Kurtulus, A. Can Babac, D. Bakircioglu

**PP11 Edina Baranyai** *The examination of iron and manganese retention in the aquatic food chain by atomic spectrometric methods* P. Herman, S. Harangi, M. Fehér, E. Baranyai

**PP12 Edina Baranyai** *Trace element determination of tree sap by microwave plasma atomic emission spectrometry* H. Kiss, S. Harangi, E. Baranyai

**PP13 Raphael Biata** *Determination of antimony and tin in beverages using inductively coupled plasma-optical emission spectrometry after ionic liquid based ultrasonic-assisted liquid-liquid phase microextraction* N. R. Biata, L. Nyaba, J. Ramontja, N. o Mketo, P. N. Nomngongo

**PP14 Fausto Bredice** *Measurement of Laser Generated Plasma Parameters through the Perturbation caused by the plasma in a stationary electric field* F. Bredice, C. Sánchez-Aké, M. Villagrán Muniz, V. Palleschi, P. Pacheco Martínez, R. S. Mercado

**PP15 Fausto Bredice** *Temporal Evolution of the Boltzmann Plot as a Tool for the Characterization of Plasma Generated by Laser* F. Bredice, C. Sánchez-Aké, M. Villagrán Muniz

**PP16 Víctor Chubarov** *Chemical state determination by WDXRF analysis for geochemical investigations* V. Chubarov

**PP17 Victor Chubarov** *WDXRF analysis of chromium ores* V. Chubarov, A. Amosova

**PP18 Sesil Cizmeci** *Application of High-Resolution Continuum Source Molecular Absorption Spectrometry with Solid and Solution Sampling for the Determination of Fluorine in Tea Varieties and Their Infusions* S. Cizmeci, N. Ozbek, H. Tinas, S. Akman

**PP19 Stefano Columbu** *Characterization of ancient colored paintings on the lime-plaster from the "Teatro Marittimo" of Roman Hadrian's Villa (Rome, Italy)* S. Columbu, M. Lezzerini, S. Pagnotta, S. Raneri, S. Legnaioli, V. Palleschi

**PP20 Gabriella Dravecz** *Solid Sampling Determination of Pb and Cd in Black Tea Leaf by High Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry* G. Dravecz, N. Laczai, Z. Ajtony, L. Bencs

**PP21 Olivier Forni** *Results of the ChemCam Instrument on Board the MSL-Curiosity Rover: Calibration and geochemistry from minor and traces elements* O. Forni, J. Frydenvang, A. Cousin, O. Gasnault, S. Maurice, P.-Y. Meslin, A. Ollila, V. Payré, R. C. Wiens, The ChemCam Team

**PP22 Jens Frydenvang** *Quantitative major element calibration of the ChemCam instrument on the NASA Mars Science Laboratory Curiosity rover* J. Frydenvang, O. Forni, S. M. Clegg, R. B. Anderson, R. C. Wiens, A. Cousin, S. Maurice, O. Gasnault and the ChemCam Team

**PP23 Gábor Gálbacs** *Construction and initial characterization of a spatially heterodyne LIBS spectrometer* D. J. Palásti, I. Rigó, M. Veres, G. Galbács

**PP24 Gábor Gálbacs** *Investigation of apatite grains in amphibolite rock samples by laser and X-ray spectroscopy methods* P. Janovszky, F. Schubert, T. M. Tóth, G. Galbács

**PP25 Beatriz Gómez-Nieto** *Direct determination of silicon in oil-in-water emulsions by high-resolution continuum source flame atomic absorption spectrometry* B. Gómez-Nieto, M. Jesús Gismera, M. Teresa Sevilla, S. Cofrades, J. R. Procopio

**PP26 Sándor Harangi** *Method development for the determination of iAs in rice using hydride generation atomic absorption spectrometry (HG-AAS)* H. Fige, S. Harangi, M. Costedoat, J.-Pi. Lener, E. Baranyai

**PP27 Richard Hark** *Analyzing Carbonate Muds by Handheld LIBS* E. C. Rankey, R. R. Hark, C. S. Throckmorton, R. S. Harmon, A. M. Somers, K. E. Bompiani, L. M. Collins

**PP28 Jörg Hermann** *Analysis of aerosols via calibration-free laser-induced breakdown spectroscopy in helium* M. Boudhib, J. Hermann, C. Dutouquet

- PP29 Suleyman Akman** *Formation Mechanisms of Calcium Monofluoride in Graphite Furnace Molecular Absorption Spectrometry and Interactions with Competitive Elements* S. Akman, Nil Ozbek
- PP30 Alexey Ilyin** *Collisional Radiative Model for Filamentation of Tightly Focused Femtosecond Laser Pulses in Air* A. Ilyin, S. Golik, K. Shmirko, A. Mayor, D. Proshenko
- PP31 Przemysław Jodłowski** *Comparison of theoretical and experimental studies of methane adsorption on PdO/Al<sub>2</sub>O<sub>3</sub> structured catalyst* P. Jodłowski, I. Czekaj, R. J. Jędrzejczyk, D. Chleba
- PP32 Maria Knadel** *Laser Induced Breakdown Spectroscopy for Soil Specific Surface Area Estimation* M. Knadel, C. Hermansen, P. Moldrup, M. H. Greve, E. Arthur, Lis W. de Jonge
- PP33 Annarita Laricchiuta** *Thermodynamic and Transport Properties of Plasmas including Silicon-based Compounds* G. Colonna, A. D'Angola, L. D. Pietanza, M. Capitelli, F. Pirani, E. Stevanato, A. Laricchiuta
- PP34 Violeta Lazic** *Calibration strategy for quantitative LIBS measurements in extremely variable plasma conditions, and for reduction of the matrix effect* V. Lazic, A. De Ninno
- PP35 X. Chris Le** *Detection of Bacterial Pathogens in Water Using Affinity Aptamers and Inductively Coupled Plasma Mass Spectrometry* C. Hamula, F. Li, Y. Liu, Z. Wang, Q. Zhao, X. Chris Le, Xing-Fang Li
- PP36 Alessandro Lenzi** *Determination of mercury in geothermal fluids employed as sources in power plants* A. Lenzi, A. Caprai, A. D'Ulivo, M. Onor, M. Mascherpa, M. Paci, A. Bettini
- PP37 Javier Manrique** *Measurement of transition probabilities of Mn II lines by laser-induced breakdown spectroscopy* J. Manrique, C. Aragón, J. A. Aguilera
- PP38 Nikolay Mashyanov** *Thermospecies of mercury in lichens as bioindicators of air pollution* N. Panichev, M. Mathebula, K. Mandiwana, N. Mashyanov, S. Pogarev
- PP39 Cheryl McCrindle** *Food Safety implications of Polluted Water in South Africa* C. McCrindle, M. Seopela, A. Ambushe, K. Mekkonen, R. McCrindle
- PP40 Marcia Foster Mesko** *Rare Earth Elements Determination in Crude Oil and Fractions by Electrothermal Vaporization-Inductively Coupled Plasma Mass Spectrometry* F.A. Duarte, J.S. Silva, A. S. Henn, P.A. Mello, C. A. Bizzi, E. M. M. Flores
- PP41 Isabel Moreira** *Endocrine Disrupters in Dolphins from the Brazilian Coast* R. Lavandier, R. Montone, S. Taniguchi, S. Siciliano, N. Quinete, I. Moreira
- PP42 Héctor Morillas** *Micro-Raman and SEM-EDX application to evaluate the nature of cluster particles present in Secondary Marine Aerosol highly influenced by anthropogenic emissions* H. Morillas, I. Marcaida, M. Maguregui, C. García-Florentino, U. Balziskueta, J. Manuel Madariaga
- PP43 Tomáš Matoušek** *Direct Speciation Analysis of Arsenic in Wine, Beer and Apple Juice by Hydride Generation-Cryotrapping- Atomic Absorption Spectrometry* A. Fajgarová, T. Matoušek
- PP44 Agnieszka Nawrocka** *Essential and Toxic Metal Contents in Smoked Meat Products available on the Polish Market* A. Nawrocka, M. Durkalec, N. Kmiecik, A. Posyniak
- PP45 Philiswa Nosizo Nomngongo** *Determination of antimony and tin in beverages using inductively coupled plasma-optical emission spectrometry after ultrasound-assisted ionic liquid dispersive liquid-liquid phase microextraction* T.S. Munonde, N.W. Maxakato, P.N. Nomngongo
- PP46 Philiswa Nosizo Nomngongo** *Preconcentration and speciation of chromium in river water using inductively coupled plasma-optical emission spectroscopy after ultrasound-assisted magnetic solid phase extraction* T.S. Munonde, N.W. Maxakato, P.N. Nomngongo
- PP47 Karel Novotný** *Normalization of LIBS spectra using acoustic and total emission signal* K. Novotný, A. Hrdlička, E. Pospíšilová, J. Piše, P. Pořízka, J. Kaiser
- PP48 Davi F. Oliveira** *Analysis of Scale Deposition in Oil Pipes using X-Ray Microfluorescence Imaging Technique* D.F. Oliveira, C.A. Marinho, M.J. Anjos, R.T. Lopes
- PP49 Uwe Oppermann** *Determination of Heavy Metals in Beer using ICP-MS Spectrometry* U. Oppermann, L. Fromentoux, J. Knoop, J. Schram
- PP50 Nil Ozbek** *The Solid Phase Extraction of Some Trace Metals Using Graphene Nanoplatelets by HR-CS AAS* N. Ozbek, A. Baysal
- PP51 Giovanni Pardini** *Determination of Pb, Zn and Cd in soil samples by means of total reflection X-ray fluorescence analysis* F. Bilo, L. Borgese, R. Dalipi, G. Pardini, E. Marguá, L.E. Depero
- PP52 Giovanni Pardini** *Presence, mobility and bioavailability of toxic metals in soil, vegetation and streamwater around a ceased Pb-Sb factory (Sant Llorenç d'Hortons, Barcelona, Spain)* S. Mykolenko, V. Liedienov, M. Kharytonov, I. Queralt, M. Hidalgo, E. Marguá, G. Pardini
- PP53 Christian Parigger** *Electron density and temperature distribution in expanding laser-induced plasma* C.G. Parigger, G. Gautam, C. Helstern, K. Drake
- PP54 Sofia Pessanha** *The use of portable EDXRF setup with triaxial geometry for the study of liquid samples – Application to mine waters* S. Pessanha, M.L. Carvalho, E. Marguá, I. Queralt
- PP55 David Prochazka** *Enhancement of laser-induced breakdown spectroscopy signal by means of combination of pre-ablation and re-heating laser pulses* D. Prochazka, J. Klus, P. Pořízka, J. Novotný, K. Novotný, A. Hrdlička, J. Kaiser
- PP56 María del Carmen Rico Rodríguez** *Fast Detection of Adulteration in Honey using Laser-Induced Breakdown Spectroscopy and Neural Networks* M. del Carmen Rico Rodríguez, S. Manzoor, J.D. Rosales, J.O. Cáceres
- PP57 Daniel Riebe** *Calibration-free laser induced breakdown spectroscopy for the quantitative determination of soil nutrients* D. Riebe, S. Pagnotta, T. Beitz, H.-G. Löhmannsröben, V. Palleschi

- PP58 Anne-Sophie Rother** *Molecular femtosecond LIBS compared to excitations with longer pulse durations* A.-S. Rother, P. Kohns, G. Ankerhold
- PP59 Madlen Rühlmann** *Design of an online-analysis technique for the determination of major and minor nutrients in soils using double-pulse laser-induced breakdown spectroscopy* M. Rühlmann, T. Schmid, M. Ostermann, D. Büchele
- PP60 Çiğdem Arpa Şahin** *Determination of Nickel and Cobalt in Food Samples by Using Ultrasound-Assisted Solidified Floating Organic Drop Microextraction Followed By Flame Atomic Absorption Spectrometry* Ç. Arpa Şahin, İ. Andaşır, İ. Durukan Temuge, S. Bektaş
- PP61 Citlali Sánchez-Aké** *Influence of the Spot Size on ZnO Thin Films Produced by Pulsed Laser Deposition* A. Yáñez-Guzmán, A. Fernández, Citlali Sánchez Aké, T. García-Fernández, M. Villagrán-Muniz
- PP62 Carlos Sánchez-Rodríguez** *Removing interferences in organic solvents and petroleum products by hTISIS-ICP-MS/MS* C. Sánchez, F. Chainet, C. Philippe Lienemann, J. Luis Todolí
- PP63 Nick Schiavon** *Assessing the efficacy of the EDXRF/Monte Carlo Simulations approach in the analysis of ancient metal artifacts: an experimental study on artificial corroded alloy samples* N. Schiavon, E. Angelini, S. Grassini, A. Brunetti
- PP64 Mauana Schneider** *Iodine determination by high resolution continuum source molecular absorption spectrometry: A comparative between promising molecules* M. Schneider, Mao-Dong Huang, H. Becker-Ross, B. Welz
- PP65 Susanne Schröder** *Quantification of Chlorine via Molecular Emissions of CaCl in Laser-induced Breakdown Spectroscopy under Martian Conditions* D. S. Vogt, K. Rammelkamp, S. Schröder, H.-W. Hübers
- PP66 Giorgio Senesi** *Micro-Laser Induced Breakdown Spectroscopy for recognition of chemical zoning of Ti-rich garnets in thin section* G. Agrosi, P. Manzari, G. S. Senesi, G. Tempesta
- PP67 Sungho Shin** *Characterization of Signal Variation by Metal Types and Surface Conditions during Laser Induced Breakdown Spectroscopy* S. Shin, H. Jang, J. Lee, J.-H. Choi, E. Hwang, S. Jeong
- PP68 Sergey Sholupov** *Optimization of measurement technique for automated DGM determination in water* S. Sholupov, N. Mashyanov, S. Pogarev, V. Ryzhov, F. Fornai, F. Bartaloni, G. Saviozzi, C. Laschi, P. Dario, F. Pacini, G. Teti, L. Volpi
- PP69 Sergey Sholupov** *Real-time highly sensitive and selective benzene and mercury determination in air and natural gas by differential absorption spectrometry with the direct Zeeman effect*
- PP70 Panayiotis Siozos** *Substrate effect on the LIBS emission of nanometer scale thick layers* P. Siozos, S. Prasad Banerjee, N. Giannakaris, T. Sarnet, D. Konios, M. Krassas, E. Stratakis, E. Kymakis, M. Sentis, D. Anglos
- PP71 Gioacchino Tempesta** *Micro-laser induced breakdown spectroscopy of an iron meteorite* G. Tempesta, P. Manzari, G. S. Senesi, G. Agrosi
- PP72 Hande Tinas** *Determination of Lead in Flour Directly by Solid Sampling High Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry* H. Tinas, N. Ozbek, S. Akman
- PP73 Ricardo Urrutia-Goyes** *Simple PXRF Field Measurement Methodology for Trace Elements in Soil* R. Urrutia-Goyes, A. Argyraki, N. Ornelas-Soto
- PP74 Maria Goreti R. Vale** *Determination of Chromium and Cadmium in Mushroom Samples by HR-CS SS-GF AAS* J. G. César, A. V. Zmozinski, W. Boschetti, M. G. R. Vale
- PP75 Maria Goreti R. Vale** *Investigation of spectral interferences on the determination of Pb in road dust samples using high-resolution continuum source graphite furnace atomic absorption spectrometry* S.S. Fick, F.V. Nakadi, P. Smichowski, F. Fujiwara, M.G.R. Vale
- PP76 Emiliya Tomova Vasileva-Veleva** *Determination of thorium in seawater by using SeaFast matrix separation system and Isotope Dilution Inductively Coupled Plasma Mass Spectrometry* I. Wysocka, E. Vassileva
- PP77 Richard Viskup** *Measurement of Diesel Particulate Matter exhaust emissions generated from real Diesel combustion engine personal vehicles by means of Laser Induced Breakdown Spectroscopy* R. Viskup, W. Baumgartner
- PP78 Li Xue** *Single-particle Investigation of Antarctic Sea Spray Aerosols Using Low-Z particle EPMA, Raman Microspectrometry, and ATR-FTIR Imaging Techniques* Hyo-Jin Eom, X. Li, H. Hwang, S. Hur, Y. Gim, C. Ro
- PP79 Sang Soon Yun** *Determination of benzoic acid and sorbic acid in Vegetables* S.S. Yun, S.J. Lee, J.S. So, G. Lee, M. Kim
- PP80 Zhuoyong Zhang** *Classification of Sand Samples by Using Terahertz Time-Domain Spectroscopy and Chemometrics* P. Liu, Xin Zhang, B. Pan, M. Wei, Z. Zhang, P. de B. Harrington



## Poster Sessions III

Thursday 15<sup>th</sup> of June 17:30-19:00

**PP1 Vanessa Antunes** *Highlighting Flemish and Portuguese painting workshops differences and similarities: two paintings and two masters* V. Antunes, A. Candeias, M. L. Carvalho, C. Barrocas Dias, A. Manhita, M. J. Francisco, A. Lauw, M. Manso

**PP2 Andrea Antunes** *Characterization of polymeric biomaterial for high-resolution X-ray Imaging* A. Antunes, I. L. Ferreira, A.F.G. Monte, M. Raposo

**PP3 Marco Arruda** *Metabolomic approach investigating differences in two generation of genetically modified and non-modified soybean seeds* B. Campo, R. Galazzi, F. Santos, M. Eberlin, M. Arruda

**PP4 Marco Carlo Mascherpa** *Fourier Transform Infrared Spectroscopy in the leather quality control (LIFE14 ENV/IT/000443 LIFETAN)* M. C. Mascherpa, M. Onor, B. Campanella, A. D'Ulivo, E. Pitzalis, E. Salernitano, A. Strafella, A. Dall'Ara and E. Bramanti

**PP5 Jorge Caceres** *Megapixel multi-elemental imaging by Laser-Induced Breakdown Spectroscopy, a technology with considerable potential for paleoclimate studies* J. O. Cáceres, V. Motto-Ros, S. Moncayo, F. Trichard, F. Pelascini, G. Panczer, A. Marín-Roldán, S. Manzoora, J. Cruz, I. Coronado, J. Martín-Chivelet

**PP6 Damian Chlebda** *Evaluation of the surface intermediates during the methane catalytic combustion over non-noble catalysts by in situ NIR and 2D-COS* D. K. Chlebda, P. J. Jodłowski, R. J. Jędrzejczyk, A. Dziedzicka, D. Pawcenis, J. Łojewska

**PP7 Adolfo Cobo** *Automatic classification of metal alloys from their LIBS spectra and its robustness against spectrometer decalibration* A. Cobo, A. Picón, M. Martínez, C. López-Sarachaga, Z. Amondarain, J. M. López-Higuera

**PP8 David Day** *Quantification of Carbon in Steel using Handheld LIBS* B. Connors and David R. Day

**PP9 Alessandro De Giacomo** *Nanoparticles-Enhanced Laser-Ablation ICP-MS Of Metals* F. Mastroiocco, L.C. Giannossa, C. Koral, A. De Giacomo, A. Mangone

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- PP71 Citlali Sánchez-Aké** *Influence of the Spot Size on ZnO Thin Films Produced by Pulsed Laser Deposition* A. Yáñez-Guzmán, A. Fernández, C. Sánchez Aké, T. García-Fernández, M. Villagrán-Muniz

## **The sources, progress and frontiers of an exciting technology: Laser-Induced Breakdown Spectroscopy.**

Javier Laserna\*<sup>A</sup>

<sup>A</sup>Departamento de Química Analítica, Universidad de Málaga, 29071 Málaga, Spain..

\*laserna@uma.es

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*ABSTRACT: Laser induced breakdown spectroscopy (LIBS) is currently considered one of the most active research areas in the field of analytical spectroscopy. LIBS has emerged as a powerful alternative for chemical analysis in a wide front of applications, from geological exploration to industrial inspection, from environmental monitoring to biomedical and forensic analysis, from cultural heritage to homeland security. Development of LIBS instruments with extended capabilities for energy dosage to the sample using ultrashort laser pulses has been undertaken which have permitted a better understanding of the underlying issues of LIBS –notably, laser interaction with matter, plasma dynamics and properties. Significant progress in chemical information from the traditional ns monopulse ablation to multipulse, multiwavelength excitation has occurred in the last decade. These advances have resulted in substantial improvements in detection limits and method precision and accuracy. While LIBS certainly has practical utility in many laboratory-based chemical measurements, the true potential of this technology becomes apparent when it is used for applications inaccessible to more conventional analytical techniques. Underwater LIBS analysis and inspection of the elemental composition of distant objects constitute examples of the exclusive capabilities of LIBS. In this lecture an overview of LIBS from the original concepts to the current technology is presented. LIBS research of relevance to contemporary chemical analysis including both innovative performance breakthroughs and emerging applications will be discussed.*

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## Unraveling genetically modified organisms through mass spectrometry

Marco Aurélio Zezzi Arruda\*<sup>A,B</sup>

<sup>A</sup>GEPAM group, Institute of Chemistry, Analytical Chemistry Department, University of Campinas – Unicamp, 13083-970, PO Box 6154, Campinas, São Paulo, Brazil; <sup>B</sup>National Institute of Science and Technology in Bioanalytics – INCTBio, Institute of Chemistry, Analytical Chemistry Department, University of Campinas – Unicamp, 13083-970, PO Box 6154, Campinas, São Paulo, Brazil.

\*zezzi@iqm.unicamp.br

**ABSTRACT:** *The introduction of exogenous genes is successfully attained into plants since the 80's, and the first report [1] is that one conferring the resistance of the soybeans to the glyphosate, the most sealing herbicide in the word. This strategy make possible those so called genetically modified organisms (GMOs), showing a good appeal to sustainability, once the GMOs present enhanced characteristics as high amount of fibers, proteins, are resistant to pests and/or insets, among others [2]. Additionally, the production is exponentially increasing, so that 170 M hectares are nowadays related to crops engineered in at least 28 countries [2]. Inside the context of GMOs, since some years ago, our research group is deeply interested in evaluating the effects that the genetic modification confers to the plant. Then, we are applying a diversity of strategies and techniques, focusing not only on comparative studies between engineered plants or not, but also evaluating different generations of such plants and the cultivation in the presence of nanoparticles. Then this work summarizes some of our comparative studies involving GMOs. For this purpose, mass spectrometry-based techniques, such as ICP-MS, LA-ICP-MS in the imaging mode, ESI-MS/MS, and FT-ICR-MS are applied for investigating some aspects regarding soybean [Glycine max (L.) Merrill] seeds and plants concerning metals, bioaccessibility, (metallo)proteins, metabolites and stress [3-6]. All the results and studies emphasize the importance of the spectrometry-based platforms for acquiring reliable and useful results, which can be used not only for unraveling some facets of such organisms after genetic modification, but also for improving the area of engineered crops.*

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## NICE-OHMS and NICE-AAS

### Frequency Modulated Cavity Enhanced Spectroscopic Techniques for Sensitive Detection of Molecules and Atoms down to $10^{-14} \text{ cm}^{-1}$ Principles, Current Status, and Prospects

Thomas Hausmaninger<sup>A</sup>, Gang Zhao<sup>B</sup>, Isak Silander<sup>A</sup>, Weiguang Ma<sup>B</sup>, Ove Axner<sup>\*A</sup>

<sup>A</sup> Department of Physics, Umeå University, S-901 87 Umeå, Sweden; <sup>B</sup> State Key Laboratory of Quantum Optics and Quantum Optics Devices, Institute of Laser Spectroscopy, Shanxi University, Taiyuan 030006, China.

\*ove.axner@umu.se

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**ABSTRACT:** Noise-immune cavity-enhanced optical heterodyne molecular spectrometry (NICE-OHMS) is a powerful technique for detection of molecular compounds in gas phase. It is based on a combination of frequency modulation spectroscopy (FMS), for reduction of noise, and cavity enhancement (CE), for prolongation of the interaction length. By choosing the modulation frequency equal to the free-spectral range (FSR) of the cavity all spectral components of the modulated light will be transmitted through their own cavity mode. By this, any frequency fluctuation between the laser and the cavity modes will cause identical attenuation and dispersion of all light components. Since the FMS signal is given by various combinations of differences of these, it will be unaffected by such fluctuations. This is referred to as “noise immunity” and implies that detection can be made as if the cavity would not be there. The technique has the ability to detect a wide variety of signals: owing to the use of FMS, it can measure both absorption and dispersion signals; due to the presence of high intensity counter-propagating beams inside the cavity, it can detect both sub-Doppler (sD) and Doppler-broadened (Db) signals; and, finally, in order to reduce low-frequency noise or to remove the Db background on which the sD signals reside, wavelength modulation can additionally be applied. All this implies that the technique can be used for a variety of applications. The technique was originally developed for high precision frequency standard applications at JILA in Boulder, CO. In its first realization, based on a well stabilized fixed-frequency solid state laser, an absorption sensitivity of  $10^{-14} \text{ cm}^{-1}$  was demonstrated for sD detection of molecular species. This showed that NICE-OHMS has a large potential for sensitive gas analysis. However, since the locking of tunable lasers to high finesses cavities can be intricate, the technique has, for a long time, been considered too complex to be used for practical trace gas analysis. To challenge this, and to make the technique more applicable to trace gas detection, our research group has developed the NICE-OHMS technique further, with the main aim of reducing the complexity of the instrumentation while keeping as much as possible of its high sensitivity. Over the years, a variety of lasers have been used. The most powerful systems developed so far, working in the near-IR region, are based on narrowband fiber lasers and most recently whispering-gallery-mode lasers together with optical fibers and fiber-coupled components for compact realization. Using  $\text{C}_2\text{H}_2$  as the pilot species, we have meticulously characterized the technique and assessed its optimum conditions. Using a cavity with a finesse of 50 000, we have demonstrated an absorption sensitivity in the upper  $10^{-14} \text{ cm}^{-1}$  range, which corresponds to hundreds of ppq (parts-per-quadrillion) of acetylene. To reach into the mid-IR region, to address low abundant isotopologues, also systems based on optical parametric oscillators (OPOs) have been developed. This talk will provide a short description of the basic features of the technique and some of the most important results. The technique has so far not been used for analytical atomic spectrometry (AAS). A first estimate of its performance suggests though that NICE-AAS can provide detection sensitivities of Na in graphite furnaces in the zg ( $10^{-21} \text{ g}$ ) range. The prospects for, and limitations of, NICE-AAS for trace element analysis will be discussed.

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## When Anthropocene means exploiting all the elements of the periodic table: a new challenge for environmental analytical chemistry

Montserrat Filella<sup>\*A</sup>

<sup>A</sup>Institute F.-A. Forel, University of Geneva, Boulevard Carl-Vogt 66, CH-1205 Geneva, Switzerland

<sup>\*</sup>Montserrat.filella@unige.ch

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*We are now using minerals and metals in greater quantities than ever before. Since 1990 the extractive production of many metals has grown by several orders of magnitude. The rate of use has particularly increased for metals used in high-tech applications, with more than 80% of the total cumulative production of some elements (REE (rare earth elements), PGE (Pt group elements), In, Ga) having taken place since 1980. At the same time, materials have become more complex. New technologies, such as those needed for modern communication and computing and the production of clean energy, require the use of many different elements with the result that we are using more of the periodic table than in the past.*

*We are now discovering, with surprise, that we do not know much about the environmental chemistry and the ecotoxicological and human toxicity of many elements of the periodic table which, even if used since 'always', are now becoming "contaminants of emerging concern". The research in the field will eventually result in regulatory action to establish environmental guidelines or criteria to ensure adequate protection when needed. However, all the studies involved in this process require adequate analytical methods and we are also discovering, with dismay, that for many elements and matrices they do not exist. Since the 'emergence' of the awareness of emerging contaminants with Rachel Carson and her 1962 book "Silent Spring", emerging pollutants have been a major driving force for analytical chemistry, mainly in the field of organic micropollutants. Now a strong effort is needed in the 'inorganic side', beyond legacy pollutants such as Pb, As and Hg.*

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## Arsenic Speciation and Arsenic Binding to Proteins

Qingqing Liu, Xiufen Lu, Hanyong Peng, Aleksandra Popowich, Zhixin Wang, Xiaowen Yan, Xing-Fang Li, and X. Chris Le\*

Analytical and Environmental Toxicology Division, Department of Laboratory Medicine and Pathology, Faculty of Medicine and Dentistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G3

\*E-mail: xc.le@ualberta.ca

*Arsenic is one of the most important environmental agents causing chronic human disease. A wide variety of adverse health effects, including bladder, lung, and skin cancers, have been attributed to chronic exposure to arsenic. Many arsenic species undergo metabolism, and the toxicities of arsenic metabolites vary by several orders of magnitude. To facilitate studies of arsenic speciation, we and others have developed several chromatography and mass spectrometry techniques that enable quantitative determination of a variety of arsenic species. An example is the simultaneous detection with both inductively coupled plasma mass spectrometry (ICPMS) and electrospray ionization tandem mass spectrometry (ESI-MS/MS) after high performance liquid chromatography (HPLC) separation. This presentation will show several applications of these techniques to studies of exposure, metabolism, and health effects of arsenic species.*

*Arsenic is also used in the successful treatment of acute promyelocytic leukemia (APL). Binding of arsenic to the promyelocytic leukemia fusion protein (oncoprotein) is a key event of the successful treatment. Therefore, identification of other arsenic-binding proteins is important for developing arsenic-based therapeutics for other cancers. We describe a strategy for the capture and identification of arsenic-binding proteins in living cells. An affinity capture technique, using click chemistry and mass spectrometry, enabled identification of arsenic-binding proteins in human cell lines. Applications of the technique are demonstrated using the A549 human lung carcinoma cells. We are able to capture and identify 48 arsenic-binding proteins in A549 cells. Among the identified proteins are several antioxidant proteins (e.g., thioredoxin, peroxiredoxin, peroxide reductase, glutathione reductase, and protein disulfide isomerase) and glyceraldehyde-3-phosphate dehydrogenase. Studies of arsenic binding to some of these proteins and the consequent enzymatic inhibition suggest that these proteins could be potential molecular targets that play important roles in cancer treatment and in arsenic-induced health effects.*

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## The plasma characteristics and sample behavior in the ICP revealed through computer modeling.

Annemie Bogaerts\*<sup>A</sup>, Maryam Aghaei<sup>A</sup>

<sup>A</sup>Research group PLASMANT, Department of Chemistry, University of Antwerp, Universiteitsplein 1, Antwerp, Belgium.

\*annemie.bogaerts@uantwerpen.be

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*ICP-MS is widely used for many applications. Nevertheless, the underlying plasma characteristics and the behavior of the sample material are not yet fully understood. We try to obtain a better insight in the underlying processes by means of computer modeling. In the last 5 years, we developed a comprehensive model, which simulates the ICP torch connected to a MS sampling cone, considering the large pressure drop from upstream to downstream (i.e. 1 atm to 1 torr). I will explain the model, including the assumptions made, the equations to be solved and the input data and boundary conditions of the model. The model describes the gas flow behavior inside the ICP, as well as typical plasma characteristics, such as plasma temperature and electron density. Besides, the effect of the injection of analyte material is accounted for. We focus on elemental particles, as relevant for LA-ICP-MS. The inserted elemental particles are followed throughout the ICP, up to the evaporation step, and we also include ionization of the vapor atoms, taking Cu as a case study. The model allows us to trace the particles, and to determine their position, their phase (liquid, vapor or ionized), velocity and temperature, both in the ICP torch and at the sampler orifice. Thus, we can determine the shape and position of the ion clouds, originating from either the Ar flow or the inserted sample material, which is of interest for both OES and MS studies. Finally, we can obtain information on the fraction of Cu<sup>+</sup> ions passing the sampling cone, with respect to the amount of Cu injected into the ICP. I will show typical calculation results, illustrating the plasma characteristics and gas flow patterns, as well as the sample transport, evaporation and ionization, to indicate what type of information can be obtained from the model, and how modeling can contribute to a better insight in the underlying mechanisms and help to improve the applications. I will first show the general ICP characteristics and sample behavior at typical gas flow rates (i.e., 1 L/min injector gas, 0.4 L/min auxiliary gas, and 12 L/min outer gas flow rate), a plasma power of 1000 W, and Cu particles of 1 µm diameter, injected at a mass loading flow rate of 100 ng/s through an injector inlet of 1.5 mm diameter. Subsequently, I will present the effect of the sampler orifice diameter and position, the injector inlet diameter and position of particle injection (including on-axis and off-axis injection), the gas flow rates and plasma power, as well as the particle diameter (in the range of 0.1 – 100 µm) and particle mass loading flow rate (in the range of 1 ng/s – 500 µg/s), on the ICP characteristics and on the behavior of the sample material, to illustrate how modeling can help to elucidate the optimal conditions for improved analytical performance*

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## Solid Matrix Transformation as a Sample Preparation Method for Laser Induced Breakdown Spectroscopy and Laser Ablation Inductively Coupled Plasma Analysis

Richard E. Russo<sup>\*A,B</sup>, Jay W. Grate<sup>C</sup>, Jhanis J. Gonzalez<sup>A,B</sup>, Matthew J. O'Hara, Cyndi M. Niver, David W. Koppenaal<sup>C</sup>, George C-Y Chan<sup>A</sup>, Xianglei Mao<sup>A</sup>, Vassilia Zorba<sup>A</sup>

<sup>A</sup> Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California, USA; City, Country;

<sup>B</sup> Applied Spectra, Inc. 46665 Fremont Blvd, Fremont, California, USA; <sup>C</sup> Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, Washington, USA

\*rerusso@lbl.gov

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**ABSTRACT:** Laser ablation (LA) as a sampling approach with analysis using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Laser Induced Breakdown Spectroscopy (LIBS) is commonly promoted as a 'no sample preparation' approach when dealing with solids directly. For many applications, direct solid sample analysis without sample preparation is viable. Many international researchers have shown how laser parameters such as wavelength, pulse duration, energy and spot size play a role on the accuracy and precision of analysis. It also has been shown that femtosecond laser ablation can significantly reduce matrix-matching requirements needed for calibration. Achieving good qualitative and semi-quantitative analysis is practically routine with today's instruments. However, in cases where standards are needed for quantitative analysis, but do not exist, a means for standardization must be established. Some efforts have included simultaneous desolvated liquid with laser ablation, nano-particle coating of the sample, and others. The success of MALDI is the process of creating a standardized matrix, so the sample is now just a small part of the total composition, similar to digesting a portion of a solid into a liquid, in which case the liquid is the main sample that is injected into the ICP. Without digesting the sample in acid, is there some nominal effort to prepare the sample before analysis similar to MALDI, which would be suitable for LA in both ICP and LIBS analyses? We are studying and developing a new direct solid transformation approach that allows a consistent matrix that can contain spikes for isotope dilution or internal standards. Our approach also produces a 'standardized' matrix – the sample is no longer the matrix, but a part of a common matrix. The approach is more straightforward than conventional acid digestion or lithium borate type fusion processes. This presentation will describe our initial studies transforming NIST glass and pitchblend samples from their original matrix into a modified matrix. The modified matrix also will contain several elements that are tested for their suitability as an internal standard including isotope dilution.

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## Solid Matrix High-resolution Continuum Source Absorption Spectrometry can do it...

Bernhard Welz\*

Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis, SC, Brazil

\*rerusso@lbl.gov

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**ABSTRACT:** This title should say that this technique can do (almost) everything that you might expect from a high-resolution absorption spectrometer that works with a high-intensity continuum radiation source and a linear CCD array detector in the spectral range of a conventional atomic absorption spectrometer (AAS). First of all, the use of a continuum source with a CCD array detector opens the (spectral) window, and you can see the spectral environment of the analytical line at high resolution – and if you want in three dimensions. This greatly facilitates method development, and discovery and removal of spectral interferences. The instrument is also equipped with two unsurpassed background correction systems, one of which corrects automatically for any ‘continuous’ background, i.e., background that only changes with time, not over the wavelength, and this measurement and correction of background is strictly simultaneous with the measurement of atomic or molecular absorption, avoiding any artifacts due to rapidly changing background absorption. The other correction system is called least squares background correction (LSBC), which corrects for background with a fine structure due to the absorption of diatomic molecules, one of the most notorious spectral interferences in line source AAS. Due to the use of a high-intensity continuum radiation source with essentially the same intensity between 190 and 900 nm, all absorption lines within this range become available for measurement with the same intensity (not sensitivity!). This makes possible using secondary lines of lower sensitivity without compromises. This includes the possibility of determining more than one element simultaneously, if a secondary line of another element falls within the spectral range of the CCD detector. Obviously, the same atomizers, i.e., flames and furnaces are used in high-resolution continuum source AAS (HR-CS AAS) as in conventional line source AAS; however, one technique appears to have gained a lot from the improvements brought about by HR-CS AAS, and that is direct solid sample analysis using graphite furnace AAS. The number of papers that have been published within the last decade about the application of direct solid sample analysis of in part extremely complex samples in a graphite furnace using aqueous standards for calibration, i.e., without any interference, is impressive. This means that this technique has become extremely robust with the introduction of HR-CS AAS. Probably the most important innovation that has been brought about by this technique is the possibility to determine non-metals via their diatomic molecules. Due to the excellent resolution of HR-CS AAS, the rotational fine structure of the molecular bands is well resolved, and the individual rotational lines can be used in the same way for absorption measurements via molecular absorption spectrometry (MAS) as atomic lines. This way elements such as phosphorus, sulfur and the halogens can be added to the list of elements that can be determined by this technique.

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## Laser-induced breakdown spectroscopy: personal reminiscences of a long-lasting interaction

Nicoló Omenetto\*

Department of Chemistry, University of Florida, Gainesville, FL, USA

\*nicolo.omenetto@chem.ufl.edu

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*This lecture will review my personal experience with the technique of Laser-induced Breakdown Spectroscopy (LIBS). In view of my career-long sparkling interest in the analytical and diagnostic aspects of atomic emission, absorption and fluorescence spectroscopy with laser excitation, it was only natural to add another spark to the scenario. The talk will cover our first LIBS experiments with atmospheric aerosols, followed by a variety of research projects, such as ground state atomic absorption imaging, time-resolved ionic fluorescence in the plasma, and calibration-free analysis. I used to name several of these experiments “toccata e fuga”(touch and go), in the sense that, while working on one project, other (sometimes unexpected) findings triggered continuously new research directions to explore, leaving the original project incomplete. Finally, I will try to convey my overall evaluation of LIBS, which is still witnessing many evolutionary developments but has reached the stage of maturity that justifies its place among the other analytical “superstars”.*

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## Latest developments in understanding the plasma processes in analytical glow discharge optical emission and mass spectrometry

Sohail Mushtaq<sup>\*A</sup>, Edward Steers<sup>A</sup>, Volker Hoffmann<sup>B</sup>, Zdenek Weiss<sup>C</sup>, Martin Kasik<sup>D</sup>, Silke Richter<sup>E</sup>, Juliet Pickering<sup>F</sup>

<sup>A</sup>London Metropolitan University, 166-220 Holloway Road, London, N7 8DB, UK; <sup>B</sup>IFW Dresden, Institute for Complex Materials, Dresden, Germany; <sup>C</sup>LECO Instrumente Plzeň spol. s r. o., Plaská 66, 32300 Plzeň, Czech Republic; <sup>D</sup>EAG Laboratories, 103 Commerce Blvd., Liverpool, NY 13088, USA; <sup>E</sup>Bundesanstalt für Materialforschung und -prüfung (BAM), Richard-Willstätter-Straße 11, 12489 Berlin, Germany; <sup>F</sup>Blackett Laboratory, Imperial College, London, SW7 2BW, UK

\*smushtaq@live.co.uk

*Glow discharge spectroscopy (GDS) is used for the analysis of bulk and layered samples in the electronic, automotive, aerospace, photovoltaic and other industries. The sample to be analysed forms the cathode of a low current (1-40 mA) glow discharge (GD) in a noble gas, (usually Ar) at a low pressure, typically 50-500 Pa. Either the optical or mass spectrum is recorded (Optical emission spectroscopy –OES or mass spectrometry -MS). Such plasmas are not in thermal equilibrium and the various processes occurring in the plasma cannot be described in terms of characteristic temperatures. The degree of ionization and relative populations of the excited levels of atoms and ions depend on various processes such as electron impact excitation / ionization, Penning excitation / ionization and Asymmetric Charge Transfer (ACT). The presence in the plasma of a small amounts of molecular gas (e.g. H<sub>2</sub>, O<sub>2</sub> or N<sub>2</sub>), possibly trapped in the sample or source or formed when, e.g., an oxide is sputtered, can cause major changes in the number densities of plasma gas ions and metastable atoms and so affect the intensities of spectral lines (in GD-OES) and the populations of sample ions (in GD-MS). A deep understanding of the contributions of the various excitation processes is a challenging goal and investigations with various cathode materials and plasma gases are needed to obtain this understanding. The progress achieved recently in this area has been reflected in analytical methodology, thereby improving the performance of GDS in analytical applications.*

*The majority of experimental investigations into the roles of the various excitation / ionization processes have been made using OES. Theoretical studies have also been made and Bogaerts has published data on the relevant interactions when molecular gases are present in a discharge. However, it is not possible to calculate the contributions of all the interactions and processes in the plasma. There is no substitute for experimental work. GD-MS can provide additional information on the processes occurring and problems encountered in GD-OES and vice-versa. We have made major advances in the understanding of plasma processes already obtained from GD-OES by using various samples, gases and gas mixtures in several commercial GD-MS instruments. For the most profitable results, the experimental conditions for GD-OES and GD-MS work must be as similar as possible.*

*In this talk involving both OES and MS investigations, the latest developments by the LondonMet GD research group in understanding the roles of the various GD plasma processes will be discussed. Particular attention will be paid to processes very recently identified in analytical glow discharges such as ACT processes involving molecular ions, (H<sub>2</sub><sup>+</sup>, O<sub>2</sub><sup>+</sup>, or N<sub>2</sub><sup>+</sup>), and the Charge Transfer and Ionization (CTI) process.*

# Evolution of EMSLIBS, from regional meeting to a global event

Mohamed Abdel Harith\*

National Institute of Laser Enhanced Science, Cairo University, Egypt

\*mharithm@staff.cu.edu.eg

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*ABSTRACT: The historical development of the Euromediterranean Symposium on Laser Induced Breakdown Spectroscopy (EMSLIBS) will be reviewed. The idea behind the organization of this symposium has been initiated during the first LIBS conference held in Tirrenia, in the vicinity of Pisa, in November 2000. The first symposium faced lots of difficulties in its organization in Cairo, Egypt due to the global political situation in September 2001. However, the conference has been successfully organized on a relatively small scale in November of the same year. The following symposia have been grown up significantly as for the number of participants and their countries. All EMSLIBS conferences have been documented in special issues of reputable scientific journals, especially Spectrochimica Acta B in which 6 out of 8 symposia have published their papers.*

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# *Nanotech Session*

## ***Nanotech I***

*(Mon. 12<sup>th</sup> of June, h. 9.45-10.45)*

## **QQQ-ICP-MS hyphenations for the characterisation of manufactured nanomaterials in complex matrices: from size-based speciation to counting**

H. Goenaga Infante\*, Susana Nunez, Dorota Bartczak

LGC Limited, Queens Road, Teddington, Middlesex TW11 0LY, United Kingdom  
of Medicine and Dentistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G3

\*Heidi.Goenaga-Infante@lgcgroup.com

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*Over 1300 consumer products, ranging from cosmetics and food additives through to paints or clothing, currently available on the market contain nanoparticles, with estimated global revenue worth €30 billion in 2015 [1]. Despite such widespread use, regulations concerning commercial use of nanomaterials have only recently started to emerge. One of their key requirements is to indicate the presence of nanomaterial, more specifically, a material containing 50% or more particles with one or more external dimensions in the size range between 1-100 nm [2]. Despite such requirements, the availability of metrologically validated methods for number-based characterisation of nanomaterials in complex samples is a current challenge. Such methods would be invaluable to support regulatory and scientific assessment of potential hazards and impact of nanomaterials on human and the environment, as well as development of standardised protocols for toxicological screens. Since health benefits and/or possible toxic effects of certain nanomaterials may depend on their chemical physicochemical properties, there is an urgent need for development of reference methods and reference materials (RMs) from simple solutions (e.g., used for method development and instrument calibration) to complex biological matrices (for method validation). Such reference methods and RMs will be invaluable tools for measurement quality assurance, product quality control and the production of new and more efficacious products. This lecture will provide insights into the current metrological challenges associated with the characterisation of manufactured nanomaterials in complex samples. This will be achieved through examples of application of on-line QQQ-ICP-MS hyphenations to (i) asymmetric flow field-flow- fractionation (AF4) for the accurate quantification of silica nanoparticles in a food sample using size-specific isotope dilution analysis and (ii) AF4 and particle tracking analysis (PTA) for the determination of number-based concentration of 80 nm silica nanoparticles (difficult to analyse by other counting techniques like single particle ICP-MS using current instrumentation) in a serum matrix. In terms of quantification, aspects affecting the achievement of high accuracy IDMS data for the mass fraction of nanomaterials in real complex samples in absence of isotopically enriched nanomaterials (used as spikes for IDMS) with the same physicochemical properties as the “native” particles will be presented. Also, the impact of rather using “like for like” behaving spikes on the overall measurement uncertainty and the requirements for reference material production will be discussed. Finally, the potential of AF4 to reliably determine number-based concentration of silica particles in the complex serum matrix by PTA with an RSD ( $n=3$ )  $\leq 5\%$  (i.e. without need for sample preparation) as well as to provide confirmatory data for number-based concentration when hyphenated to ICP-MS, will be demonstrated.*

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[2] EC Commission Recommendation 2011, 2011/696/EU, Luxembourg: European Commission

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## **The feasibility of analysis of water structure in electric field using molecular spectroscopies.**

Anna Czaderna<sup>\*A</sup>, Marcin Kozanecki<sup>A</sup>, Maciej Makowski<sup>B</sup>, Jacek Tyczkowski<sup>B</sup>

<sup>A</sup>Department of Molecular Physics, Lodz University of Technology, Zeromskiego 116, 90-924 Lodz, Poland;

<sup>B</sup>Department of Molecular Engineering, Lodz University of Technology, Wolczanska 213, 90-924 Lodz, Poland.

\*anna.czaderna@dokt.p.lodz.pl

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*ABSTRACT: In these studies we wanted to explore the possibility of analysis of distribution of hydrogen bonds and the dynamics of aqueous systems clustering. That's way, we tried to build a special micro-chamber which consist of nano-electrodes, dielectric layers, barrier layers and a working channel. The investigations have been done using molecular spectroscopies. It should be emphasized that used materials should be transparent to the laser beam and not interfere with the signal collected from the working channel. Furthermore, the barrier layer and working channel should have very poor adhesion to water. The project was funded by National Science Centre based on the number UMO-2013/09/B/ST4/03010.*

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## **Alkaline phosphatase labeled SERS active sandwich immunoassay for the detection of *E. coli*.**

Akif G. Bozkurt<sup>\*A</sup>, Gülizar G. Büyükgöz<sup>A</sup>, Mehmet Şoföroğlu<sup>A</sup>, Uğur Tamer<sup>B</sup>, İsmail H. Boyacı<sup>A</sup>

<sup>A</sup>Department of Food Engineering, Hacettepe University, Ankara, Turkey; <sup>B</sup>Faculty of Pharmacy, Gazi University, Ankara, Turkey.

\*agbozkurt@hacettepe.edu.tr

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**ABSTRACT:** In this study, we have represented that alkaline phosphatase enzyme (ALP) could be used as SERS label with nanoparticles for *E. coli* detection. While gold coated magnetic nanoparticles (MNPs-Au) displayed activity on immunomagnetic separation part, gold nanorods (Au-NRs) were modified to bind alkaline phosphatase. After immunoassay was set up with *E. coli* and nanoparticles, substrate of alkaline phosphatase was added to produce SERS-active product. At the first stage of this study, rapid and sensitive detection of ALP with Ag-NPs and Au-NRs was successfully performed. For this purpose, SERS substrates developed quantification of enzyme concentration. Au-NRs and Ag-NPs coated surfaces have gradual enhancement changes from  $10^{-11}$  to  $10^{-15}$  M ALP concentrations based on SERS measurements. The linear correlation between ALP concentrations and BCIP dimer calculated  $R^2 = 0,98839$  and  $R^2 = 0,94538$  respectively. At the second stage, we developed an alternative strategy to use ALP activity to detection of *E. coli*. The detection is based on a characteristic feature of the BCIP dimer and the quantification of its intensity from Raman Spectroscopy. Immuno affinity of antibody capturing to *E. coli* and enzyme-substrate interactions enhanced the two fold of selectivity and specificity. Under optimized conditions, it was found that the recorded SERS intensity depends on the *E. coli* concentration after the sandwich formation. The dependence was measured in *E. coli* concentration range of  $1.7 \times 10^1$ - $1.7 \times 10^6$  cfu mL<sup>-1</sup>. The sensitivity of the developed assay was investigated and the LOD and LOQ of the proposed method for *E. coli* detection were found as 3 cfu mL<sup>-1</sup> and 30 cfu mL<sup>-1</sup>, respectively.

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# *Nanotech Session*

## ***Nanotech II***

*(Mon. 12<sup>th</sup> of June, h. 11.15-13.00)*

## Vibrational Spectroscopy in Studying Microbially Synthesised Selenium Nanoparticles

Anna V. Tugarova\*, Alexander A. Kamnev

Laboratory of Biochemistry, Institute of Biochemistry and Physiology of Plants and Microorganisms, Russian Academy of Sciences, 13 Prosp. Entuziastov, 410049, Saratov, Russia

\*tugarova\_anna@mail.ru

**ABSTRACT:** Many bacteria have been shown to be capable of reducing selenium oxyanions with the formation of Se nanoparticles (Se NPs). This phenomenon attracts the attention of researchers worldwide, since selenium oxyanion reduction by soil and aquatic microorganisms is an important part of Se biogeochemical cycle in the environment. On the other hand, different biological systems (including bacteria) can be used for the synthesis of Se NPs. This belongs to the actively developing area of "green chemistry". In studying the mechanisms of Se NPs synthesis and for their characterisation, among instrumental techniques, vibrational spectroscopy (FTIR spectroscopy in various modes; Raman spectroscopy) can provide a wealth of useful information. In this lecture, a survey will be given of applications of vibrational spectroscopy techniques in studying Se NPs produced by various microorganisms. In particular, Raman spectroscopy allows various allotropic modifications of selenium in NPs to be reliably distinguished. Microbially produced reddish-orange Se NPs are mainly represented by amorphous and/or monoclinic Se modifications (see, e.g. [1,2]), which can be confirmed by other techniques (such as X-ray diffraction). FTIR spectroscopic analysis of microbially produced Se NPs is extremely sensitive to the presence of biological macromolecules (e.g., proteins, polysaccharides, lipids in varying proportions) attached to the Se NPs surface (see, e.g. [3] and references cited therein). This biomacromolecular 'shell' of varying composition makes microbially produced Se NPs different from those synthesised by chemical routes and, particularly, stabilises their aqueous suspensions (owing to negative zeta potentials of such biogenic Se NPs, largely as a result of the presence of carboxylic groups in the biomacromolecular 'shell' [3]).

Despite being actively investigated, the processes of microbial synthesis of Se NPs and their properties are not yet completely understood. Thus, further research is definitely required, including structural studies by vibrational spectroscopy techniques. Finally, it has to be mentioned that the phenomenon of microbial synthesis of Se NPs is widely applicable in various fields, such as biomedicine (particularly, in cancer treatment), bioremediation of soils and aquifers, production of biologically active food additives, packaging materials, etc.

**Acknowledgement.** This study was supported in part by The Russian Foundation for Basic Research (Grant 16-08-01302-a).

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## Characterization of metallic nanoparticles via high resolution continuum source atomic absorption spectrometry

Martin Resano\*, Esperanza García-Ruiz, Raúl Garde

Department of Analytical Chemistry, Aragón Institute of Engineering Research, University of Zaragoza, 50009, Spain

\*mresano@unizar.es

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**ABSTRACT:** *The introduction of high-resolution continuum source atomic absorption spectrometry has brought significant advantages for the progress of AAS, and has permitted the development of molecular absorption spectrometry applications as well, opening up new ways to determine non-metals,<sup>1,2</sup> and even to carry out isotopic analysis.<sup>3</sup> It seems that this technique may still have a number of surprises left. For instance, recent investigations demonstrate that it may also provide relevant information for nanoparticle (NP) research.<sup>4</sup> In fact, proper optimization of the temperature program may permit to obtain information on the chemical form (ionic or as NP) in which metals are found, since the signal profiles obtained for solutions/suspensions of ionic metals and NPs are very dissimilar.<sup>5,6</sup> In particular, proper optimization of the temperature program, using a very low heating ramp during the atomization step and in the absence of chemical modifiers, enables a fast and simple screening to be performed, since the signal profiles obtained for solutions/suspensions of ions and NPs are very dissimilar. Moreover, in the case of finding NPs, it is possible to estimate the average particle size, because this parameter is related with the time of appearance of the maximum peak height. Furthermore, it seems also possible to establish if the NPs are linked to target biomolecules, or else they are free in the solution.*

### Acknowledgements

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## Surface Enhanced Raman Scattering of Water in Dispersions of Silver Nanoparticles

Paulina Filipczak<sup>\*A</sup>, Marcin Kozanecki<sup>A</sup>, Krzysztof Halagan<sup>A</sup>

<sup>A</sup> Department of Molecular Physics, Lodz University of Technology, Zeromskiego 116, 90-924 Lodz, Poland

\*paulina.filipczak@dokt.p.lodz.pl

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**ABSTRACT:** Resonance effect is a phenomenon that strongly enhances Raman signal from the sample and strictly depends on excitation wavelength. Previous studies showed that the Raman resonance effect is present in liquid water and it directly corresponds to the supramolecular structure of liquid water. Intensity ratio of two main components of OH stretching modes with maxima around 3200 and 3400  $\text{cm}^{-1}$  (assigned to strongly and loosely hydrogen-bonded water molecules respectively) depends on the excitation wavelength in the visible range [1]. Noble metal (gold, silver) nanoparticles have been successfully applied for Surface Enhanced Raman Scattering (SERS). Significant increase in Raman signal found for many organic molecules adsorbed on expanded metal surface put attention on SERS as a very sensitive analytical technique allowing to study single molecules. Because of this fact, currently, SERS technique is more willingly used in interesting studies on the field of medicine, biology, biochemistry or crystallography. In this work, SERS effect for water molecules in aqueous dispersions of silver nanoparticles (AgNPs) is presented. An enhancement of low frequency component in OH stretching vibrations region (3200  $\text{cm}^{-1}$  band) in Raman spectrum of liquid water attributed to strongly structured water was observed. An enhancement factor was found to be at least  $10^6$ - $10^7$  for excitation wavelength 514.5 nm and AgNPs average size of  $34 \pm 14$  nm. Influence of temperature on studied phenomenon was also investigated. Experimental results were complemented by simulation studies about solvent motion (water) nearby obstacle (silver nanoparticle). Presented results are the first report on the SERS found for inorganic molecules - water interacting with silver nanoparticles. [1] M. Pastorczyk, M. Kozanecki, J. Ulański J. Phys. Chem. A, 2008, 112, 10705-10707.

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## CE-ICP-MS as a platform to differentiate the speciation changes of various theranostic metalonanomaterials in human serum.

Magdalena Matczuk\*<sup>A</sup>, Joanna Legat<sup>A</sup>

<sup>A</sup>Chair of Analytical Chemistry, Faculty of Chemistry, Warsaw University of Technology,  
Noakowskiego 3 Warsaw, Poland

\*mmatczuk@ch.pw.edu.pl

**ABSTRACT:** Metalonanomaterials (MNMs) possess unique optoelectronic and magnetic properties that make them highly promising as therapy and diagnostics (theranostics) tumor agents. The in-vivo fate of MNMs and particularly, their route from the point of administration to the targets is closely related to interactions with proteins present in the bloodstream. After a decade of research, there is still a lack of knowledge of the exact functions of proteins in MNMs mechanism of action. Therefore, it is acute need for developing more efficient analytical techniques to study protein-mediated speciation of MNMs. The aim of this contribution is the development of an analytical methodology, which will be used for characterization of the medicinally-active MNMs interactions with serum proteins. Electrophoretic techniques become more and more popular in the analysis of bio-behavior of nanomaterials. However, with common UV detection they do not allow for monitoring relevant speciation changes of MNMs. Therefore, we have selected as the method of choice capillary electrophoresis hyphenated to inductively coupled plasma mass spectrometry (CE-ICP-MS). This combined methodology takes advantages of high resolution potential of CE separation and sensitivity and specificity of ICP-MS. These benefits provided the possibility to investigate protein–MNMs interactions under mild, species-friendly conditions, at low concentrations, and using small sample volumes. In this study the speciation changes of gold nanoparticles<sup>1</sup>, gold nanorods and CdSeS/ZnS quantum dots<sup>2</sup> in serum environment were investigated. Due to the application to the experiments the various types of nanomaterials with different sizes, shapes, surface functionalization and doses it was possible to assign the parameters which crucially influence protein coronas formation in human serum. For example, in case of gold nanoparticles, the parameter which determines the interactions with distinct serum proteins was the size of nanomaterial. Summarizing, CE-ICP-MS technique was the first time successfully applied as a platform specified to separate the protein-MNMs conjugates from bare MNMs and to differentiate their trafficking on the way to cell targets.

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## Spectroscopic characterization of second-generation nanostructured antimicrobials

Nicoletta Ditaranto<sup>\*A</sup>, Maria Chiara Sportelli<sup>A</sup>, Rosaria Anna Picca<sup>A</sup>, Luigia Sabbatini<sup>A</sup>, Nicola Cioffi<sup>A</sup>

<sup>A</sup>Dipartimento di Chimica, University of Bari, via Orabona 4, 70125 Bari, Italy

\*nicoletta.ditaranto@uniba.it

**ABSTRACT:** Nanoantimicrobials based on metals (Ag, Cu, Zn) and their oxides are widely proposed as bioactive agents with low environmental and human toxicity for a number of applications, including food packaging, biomedicine, automotive and textile industries. The most desired nanoantimicrobials release metal species in a controlled manner and they eventually slow down or inhibit at all the growth of bacteria or other pathogenic microorganisms. In recent years, the authors have developed and characterized a number of different nanoantimicrobial systems capable to exert a controlled release of metallic ions into aqueous solutions [1-3] without generating a significant leaching of whole nanoparticles into the same contact media [4]. Antibacterial ionic species released by transition metal nanophases such as silver, copper and zinc oxide, provide an ideal alternative route to fight bacterial resistance towards conventional disinfecting agents. Electrochemical methods, in particular, have been used for more than a decade to produce bioactive core-shell nanocolloids, which can be used as water-insoluble nano-reservoirs providing an excellent tuning of ionic release. Laser Ablation synthesis in liquid media, wet-Chemical synthetic routes and vacuum methods such as Ion Beam sputtering, provide complementary materials with interesting antimicrobial properties. Nanoantimicrobials were investigated in several industrially relevant cases with the aim of producing surfaces with antimicrobial properties. In all cases, x-ray photoelectron spectroscopy was used to evaluate the chemical speciation and elemental composition of pristine NPs and final materials, providing useful information about the synthesis process, as well as the storage, and processing conditions. Atomic absorption spectroscopy was used to investigate the metal ions release from the modified surfaces and industrial products. Analytical spectroscopy results were matched with antimicrobial tests, to demonstrate the growth inhibition for different classes of microorganisms. Different approaches to second generation nanoantimicrobials, e.g. to those materials combining antibacterial efficiency and nanosafety issues, will be critically discussed, based on spectroscopic, morphological, release and bioactivity evidences.

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# *Nanotech Session*

## ***Nanotech III***

(Mon. 12<sup>th</sup> of June, h. 14.45-15.45)

## Interdisciplinary synchrotron radiation based X-ray spectrometry applications using the IAEA multi-technique instrument operated at the XRF beamline of Elettra Sincrotrone Trieste.

Andreas-Germanos Karydas<sup>\*A, B</sup>, Mateusz Czyzycki<sup>A, C</sup>, Alessandro Migliori<sup>A</sup>, Juan José Leani<sup>A, D</sup>, Janos Osan<sup>A, E</sup>, Nikita Vakula<sup>A</sup>, Mladen Bogovac<sup>A</sup>, Pawel Wrobel<sup>A, C</sup>, Iain Darby<sup>A</sup>, Ralf Bernd Kaiser<sup>A</sup>

<sup>A</sup>Nuclear Science and Instrumentation Laboratory, International Atomic Energy Agency (IAEA) Laboratories, A-2444 Seibersdorf, Austria; <sup>B</sup>Institute of Nuclear and Particle Physics, NCSR “Demokritos”, 153 10 Aghia Paraskevi, Athens, Greece; <sup>C</sup>AGH University of Science and Technology, Al. A. Mickiewicza 30, 30-059 Krakow, Poland; <sup>D</sup>IFEG, National Scientific and Technical Research Council (CONICET). X5000HUA, Cordoba, Argentina; <sup>E</sup>Hungarian Academy of Sciences, Centre for Energy Research, 1525 Budapest 114., P.O. Box 49., Hungary

\*karydas@inp.demokritos.gr

**ABSTRACT:** The International Atomic Energy Agency (IAEA) operates jointly with the Elettra Sincrotrone Trieste (EST) a multi-technique X-ray spectrometry end-station [1-3] at the X-ray Fluorescence (XRF) bending magnet beamline [4]. The facility is accessible to end-users since the beginning of 2015 through the established peer-review process of EST. Through this collaboration the IAEA promotes and supports synchrotron based experiments and training activities by research groups from Member States with limited previous experience and resources to access synchrotron radiation facilities. Currently, various research programs within the IAEA Coordinated Research Project (CRP) framework are in progress. The research areas of interest include characterization of nano-structured materials, materials in solar cells, characterization and speciation of environmental samples [5, 6] (airborne particulate matter, water samples, suspensions, coal fly ash), study of essential or toxic elements in plants to develop/improve biofortification, phytoremediation and phyto-mining techniques, speciation of trace elements in human tissues for cancer studies, advanced materials for preventive conservation of stone monuments, study of ancient technologies of manufacture, and systematic measurement and re-evaluation of X-ray fundamental parameters. The EST-IAEA X-ray spectrometry facility offers advanced analytical features available to limited number of synchrotron radiation facilities worldwide, namely to perform XRF measurements at different excitation or detection geometries (TXRF, GIXRF, GEXRF) combined with X-ray absorption (XANES and EXAFS) or X-ray reflectometry (XRR) measurements, supporting a comprehensive characterization of different kind of materials. Results obtained from interdisciplinary applications are reported and discussed highlighting the analytical capabilities and the perspectives for further exploitation of this new X-ray spectrometry facility.

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## Development of HPLC-ICP MS Method for Separation and Determination of Nano and Ionic Forms of Gold and Silver

Julita Malejko, Natalia Świerżewska, Beata Godlewska-Żyłkiewicz\*

Institute of Chemistry, University of Białystok, 15-245 Białystok, K. Ciołkowskiego 1K, Poland.

\*bgodlew@uwb.edu.pl

**ABSTRACT:** Metal-based nanoparticles have attracted increasing attention and found plenty of scientific, industrial and commercial applications in recent years. Gold nanoparticles (AuNPs) are widely applied in electronics, sensors, solar cells, and catalysis. AuNPs are also used for biomedical applications, like radiotherapy, cancer therapy or as drug carriers. Food supplements and cosmetics labelled to contain nanogold (e.g. lotions, skin creams, toothpastes, and soaps) are commercially available. Silver nanoparticles (AgNPs) have a broad spectrum of antimicrobial activity and therefore are incorporated into various consumer products, such as anti-odour sportswear, underwear, socks, disinfecting sprays, food contact materials, washing machines, pillows and mattresses, toothbrushes, water filters, cosmetics. Due to increasing applications of nanomaterials in daily life and thus increasing exposure to them, concerns have been raised about their safety. Speciation analysis of nano and ionic forms of metal is essential when assessing the potential impact of nanoparticles on human health and the environment. As a consequence, analytical techniques are urgently required for the simultaneous determination of these forms in different matrices (consumer products, biological and environmental samples).

The possibility of application of high performance liquid chromatography for the separation of nano and ionic forms of gold and silver with post-column ICP-MS detection is presented in this work. Different LC columns: Nucleosil C18 column (1000 Å pore size, 7 µm particle size, 250 × 4.6 mm) and two polymeric reversed phase columns (PLRP-S 1000 Å pore size, 8 µm particle size, 250 × 4.6 mm and PLRP-S 4000 Å pore size, 8 µm particle size, 150 × 4.6 mm) as well as different compositions of the mobile phase were investigated in order to obtain good resolution and ensure the stability of gold and silver species. The separated species were determined by inductively coupled plasma mass spectrometry with using 8800 ICP-QQQ spectrometer (Perlan Technology).

This work was supported by the Polish National Science Centre (DEC-2014/15/B/ST4/04641).



## Characterization of SiO<sub>2</sub> Nanoparticles by Single Particle - Inductively Coupled Plasma – Tandem Mass Spectroscopy

Diego Pereira Leite<sup>A\*</sup>, Eduardo Bolea-Fernandez<sup>B</sup>, Ana Rua-Ibarz<sup>B</sup>, Martín Resano<sup>A\*\*\*\*</sup>, Frank Vanhaecke<sup>B</sup>, Maite Aramendía<sup>A,C</sup>

<sup>A</sup> Department of Analytical Chemistry, Aragón Institute of Engineering Research (I3A), University of Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain, <sup>B</sup> Department of Analytical Chemistry, Ghent University, Campus Sterre, Krijgslaan 281-S12, 9000 Ghent, Belgium, <sup>C</sup> Centro Universitario de la Defensa de Zaragoza, Academia General Militar de Zaragoza, Carretera de Huesca s/n, 50090 Zaragoza, Spain

\*731986@unizar.es

*Abstract: Due to their unique physical and chemical properties, the use of nanomaterials is rapidly growing over the last years. As non-metal oxides, SiO<sub>2</sub> nanoparticles (NPs) are used in a wide variety of applications, such as mechanic polishing or as additives in food and cosmetics<sup>1</sup>. The use of NPs is raising the concern about their potential effects in the environment and health. Different international directives exist (e.g. European Commission<sup>2</sup>) urging the need to characterize such materials. In this regard, Single Particle Inductively Coupled Plasma – Mass Spectroscopy (SP-ICP-MS) is a technique that provides information as elemental composition, particle size, mass concentration and size distribution. Although this technique has been strongly developed in recent years, many aspects are still susceptible of improvement<sup>3</sup>. This is the case for SiO<sub>2</sub> NPs, which determination is hampered by the occurrence of strong spectral interferences coming from ubiquitous elements present in the plasma itself. ICP – Tandem Mass Spectroscopy (ICP-MS/MS) is a powerful technique dealing with such spectral overlaps in a straightforward way<sup>4</sup>. ICP-MS/MS instruments are equipped with two quadrupoles (Q1 and Q2) located before and after an octopole collision/reaction (ORS) cell, thus enabling for a double mass selection. In the MS/MS mode, all ions with different m/z than that of the target nuclide are filtered out by Q1, thus enhancing the control over the collisions/reactions taking place in the ORS and permitting a more efficient resolution of interferences.*

*This work assesses the capabilities of SP-ICP-MS/MS for interference-free determination of SiO<sub>2</sub> NPs by using different ORS conditions, i.e. no gas, He, H<sub>2</sub>, NH<sub>3</sub> and CH<sub>3</sub>F. The reactivity of Si with the different gasses was evaluated via product ion scanning, in which Q1 was set at m/z =28, with Q2 scanning over the entire mass spectrum. Once the most suited reaction product ions were identified, the use of on-mass and mass-shift approaches was investigated. On-mass methods were used in the case of “vented mode”, He and H<sub>2</sub>, while mass-shift was found to be particularly suitable in the case of NH<sub>3</sub> and CH<sub>3</sub>F. Calibration data, capabilities for the characterization of SiO<sub>2</sub> and instrumental limits of detection and quantification were compared within this work. Additional issues, such as contamination and possible effect of using chemical resolution in the measurement of fast transient signals (dwell times < 5ms), were carefully addressed. This work demonstrates the potential of SP-ICP-MS/MS for the characterization of SiO<sub>2</sub> NPs, in spite of the strong spectral overlap and high contamination typically accompanying the determination of Si via ICP-MS.*

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# *Food Analysis Session*

## ***Food Analysis I***

(Mon. 12<sup>th</sup> of June, h. 9.45-10.45)

## Laser Induced Breakdown Spectroscopy Based Protein Assay for Cereal Samples

Banu Sezer<sup>A\*</sup>, Gonca Bilge<sup>B</sup>, Ismail Hakki Boyaci<sup>A</sup>

<sup>A</sup>Department of Food Engineering, Hacettepe University 06800, Ankara, Turkey, <sup>B</sup>Nanosens A.Ş., 06790 Ankara, Turkey

\*sezerbanu@gmail.com

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**ABSTRACT:** Proteins are the main functional components in various food products and have ability to support dietary needs. Protein content is an important quality parameter in terms of price, nutritional value and labeling of various cereal samples. It has a crucial role in determining the textural, sensory and nutritional properties of the products. Therefore, determination of protein is an important quantitative analysis in terms of quality control, accurate nutrition labeling, pricing, functional property investigation and biological activity determination, which makes it a subject of both economic and social interest. However, conventional analysis methods, namely Kjeldahl and Dumas have major drawbacks such as long analysis time, titration mistakes, carrier gas dependence with high purity, and relatively low accuracy and precision. For this reason, there is an urgent need for rapid, reliable and environmentally friendly technologies for protein analysis. The present study aims to develop a new method for protein analysis in wheat flour and whole meal by using laser induced breakdown spectroscopy (LIBS), which is a multi-elemental, fast and simple spectroscopic method. Unlike the Kjeldahl and Dumas method, it has the potential to analyze high number of samples in a considerably short time. In this study, nitrogen peaks in the LIBS spectra of wheat flour and whole meal samples with different protein contents were correlated with results of standard Dumas method with the aid of chemometric methods. Calibration graph showed good linearity with the protein content between 7.9-20.9%, and 0.992 coefficient of determination ( $R^2$ ). Limit of detection (LOD), limit of quantitation (LOQ), relative error of prediction (REP) and relative standard deviation (RSD) for ash analysis in wheat flour, whole meal values were calculated as 0.26%, 0.77%, 4.5% and 4%, respectively. The results indicated that LIBS is a promising and reliable method with high sensitivity for routine protein analysis in wheat flour and whole meal samples.

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## Control of spectral interference in must and wine analysis via high-resolution continuum source flame atomic absorption spectrometry

Wiliam Boschetti<sup>\*A,B</sup>, Luíza M.G Dalagnol<sup>A</sup>, Morgana B. Dessuy<sup>A,B</sup>, Mariana Dullius<sup>C</sup>, Maria Goreti R. Vale<sup>A,B</sup>

<sup>A</sup>Instituto de Química, UFRGS, Porto Alegre, RS, Brazil; <sup>B</sup>Instituto Nacional de Ciência e Tecnologia de Energia e Ambiente, UFBA, Salvador, BA, Brazil; <sup>C</sup>Vinícola Geisse, Pinto Bandeira, RS, Brazil.

\*wiliamcaxias@gmail.com

*The grape variety Chardonnay is widely employed in the white wine and sparkling wine production. In the last few years, the Brazilian sparkling wines have drawn the attention of consumers around the world due to their quality<sup>1</sup>. Information about the composition of must and white wine used in the sparkling wine production provides great impact in the control and improvement of the excellence of this beverage<sup>2</sup>. Thus, the use of fast and reliable analytical methods in order to determine the concentration of macro and microelements in these samples is essential. The aim of this work is the development of simple analytical methods for the sequential determination of Ca, Cu, Fe, K, Mg, Mn, Na, Rb and Zn in must and white wine via high-resolution continuum source flame atomic absorption spectrometry. A flow injection valve was used to minimize the sample consumption and to maintain the thermal stability of the flame. Eighteen Chardonnay grape samples were collected in southern Brazil and by crushing these fruits the must was obtained. A fraction of the grape juices was used to produce, through a fermentation process, the white wine. Due to the presence of particles and the large quantity of sugars, the must samples were submitted to a microwave-assisted acid digestion procedure. In this process, 3 mL of must, 3 mL of 65% (w/w) HNO<sub>3</sub> and 2 mL of 30% (w/w) H<sub>2</sub>O<sub>2</sub> were added in Teflon flasks. The white wine samples were analyzed without any pre-treatment. Analyzing the digested samples, a spectral interference of the NO diatomic molecule was observed on the analytical line of Zn (213.857 nm). In order to correct this interference using the least square algorithm a reference spectrum of NO from an aqueous solution of HNO<sub>3</sub> was evaluated; however, the NO spectrum was not generated. The interference could only be completely corrected when a "blank solution" of the acid digestion was used to generate the NO reference spectrum. Considering the presence of ethanol in the white wine samples and its influence in the sample transport and in the flame temperature, calibration curves, for quantification of these samples, were established with standard solutions in 10% (v/v) ethanol. For the must samples, only standard solutions in water were used for the calibration. The values obtained for the limits of detection and quantification were consistent with those reported in the literature. To verify the accuracy of the results, recovery tests were performed and the results varied between 91 and 106%, for all elements investigated. Therefore, the developed methods are capable to perform must and white wine analysis, providing fast, accurate and reliable results with low sample and reagent consumption.*

### Acknowledgements: CNPq

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## Elemental mass spectrometric evaluation of iron nanoparticles as an enhanced iron supplement for formula milk

Sonia Fernández-Menéndez<sup>\*A</sup>, Rafaela Regina Alves Peixoto<sup>A</sup>, María Luisa Fernández-Sánchez<sup>A</sup>, Belén Fernández-Colomer<sup>B</sup>, Marta Suarez<sup>B</sup>, Marta Costa<sup>B</sup>, Alfredo Sanz-Medel<sup>A</sup>

<sup>A</sup>Department of Physical and Analytical Chemistry, Faculty of Chemistry, University of Oviedo, Avda. Julián Clavería 8, Asturias, Spain; <sup>B</sup>Neonatology Service, Department of Pediatrics, Asturias Central University Hospital (HUCA), Aldea Cerdéño, 33011 Oviedo, Spain.

\*soniafdez@gmail.com

**ABSTRACT:** Iron is the essential trace element most abundant in the human body which participates in a wide number of physiological and biological processes. Although the absorption of dietary iron (1-2 mg/day) is regulated tightly, it is just balanced with losses. Therefore, internal turnover of iron is essential to meet the requirements for erythropoiesis (20-30 mg/day). Iron deficiency is considered the first nutritional disorder in the world and is usually the result of insufficient dietary intake of iron, poor utilization of iron from ingested food, or a combination of the two. Direct addition of iron to formula milk ("iron fortified" formulas) is an effective mean of increasing the dietary intake of iron in newborns to cover their growing needs. In general iron absorption from formula is very low compared with maternal milk. Infants fed with Fe supplemented formula still show risk of iron deficiency, despite the dose generally administered (higher than the one observed in maternal milk). The search of new Fe supplements with higher bioavailability and/or absorption than those used today (i.e. FeSO<sub>4</sub>) is currently in high demand. In this sense, the use of iron nanoparticles (NPs) is being evaluated as a new form to supplement/fortify commercial milk formulas [1].

In this work the use of Fe-NPs as a new efficient iron supplement of formula milk was evaluated in lactating rats: iron enriched stable isotopes, in combination with isotope pattern deconvolution (IPD) and Inductively Coupled Plasma (ICP-MS) methodology, previously developed [2], are used to investigate the iron absorption/bioavailability and its distribution into the three basic body compartments of Fe [functional (erythrocytes), transport (serum) and storage (liver)] in lactating rats fed with <sup>57</sup>Fe-NPs supplemented formula.

Results obtained showed that the proposed <sup>57</sup>Fe-NPs lead to a higher incorporation of the supplemented <sup>57</sup>Fe in all compartments comparing with other physicochemical forms previously studied [2]. Regarding <sup>57</sup>Fe apparent absorption, it was observed that the excretion rate of the exogenous iron administered from the NPs is related to the dose more than the physicochemical form used for iron supplementation. From the results obtained, it could be concluded as well that iron incorporation from the assayed NPs was higher than other previously assayed Fe physicochemical forms (at the same total iron levels) in some compartments (e.g. serum), still being lower than the values observed for the rats fed with maternal milk [2].

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## Evaluation of internal standardization to improve the determination of trace elements in beverages by high-resolution continuum source flame atomic absorption spectrometry

Laura Fernández-López<sup>A</sup>, Beatriz Gómez-Nieto<sup>A</sup>, M<sup>a</sup> Jesús Gismera<sup>\*A</sup>, M<sup>a</sup> Teresa Sevilla<sup>A</sup>, Jesús R. Procopio<sup>A</sup>

<sup>A</sup> Departamento de Química Analítica y Análisis Instrumental. Facultad de Ciencias. Universidad Autónoma de Madrid, C/. Francisco Tomas y Valiente 7, 28049 Madrid, Spain.

\*mariajesus.gismera@uam.es

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**ABSTRACT:** The presence and amount of trace elements in beverages influence on their organoleptic, physicochemical, nutritive and toxicological characteristic. Some metals such as copper or zinc are considered essential elements for living organisms. They are required for physiological functions and their deficiency produces disorders of the digestive, cardiovascular and nervous system and dwarfisms, hypogonadism and dermatitis. Nevertheless, an excessive intake of these elements may lead to other disorders and diseases. Other elements such as lead or cadmium are potentially harmful metals and their toxicity is recognized as a major environmental health risk. For these reasons, the determination of elements in beverages is a topic of interest in nutrition, toxicology and food safety fields. In fact, the maximum content of these elements is established in technical regulations for different beverages. The analytical methods usually employed for this purpose are based on spectrometric techniques. Among them, the methodologies based on flame atomic absorption spectroscopy can be considered the most common spectrometric methods for routine task in the laboratory. However, the differences in the chemical composition of the different kinds of beverages may produce spectral and matrix interferences in a direct analysis. For this reason, a sample pretreatment and/or the use of the standard addition or matrix-matched calibration methods are usually required to reduce interferences and achieve adequate results. The sample treatment is an additional and time-consuming process that increases the risks of sample contamination and loss of analytes. The standard addition method requires a large sample volume and it is considered time-consuming in comparison with external and internal calibration methods. In matrix-matched calibration, a solution with an adequate composition to simulate a representative matrix of the sample must be prepared. This task can be difficult because in many cases it is unknown the exact nature and amount of the components that are in each kind of sample. The aim of this work is to develop analytical methods, based on flame atomic absorption spectroscopy, that could be applied for the determination of trace elements in a large variety of beverages. For this purpose, the internal standard calibration method is used in order to reduce and minimize interferences by transport effect due to the different contents of components such as alcohol and/or sugars that are present in these samples. Bismuth, silver, nickel, ruthenium and cobalt have been evaluated as internal standard for copper, zinc and lead. The proposed methodology has been applied to analyze non-alcoholic and alcoholic beverages such as fermented beverages, distilled spirits, fortified drinks, liqueurs and creams.

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# *Food Analysis Session*

## ***Food Analysis II***

*(Mon. 12<sup>th</sup> of June, h. 11.15-13.00)*

## Laser Induced Breakdown Spectroscopy for Determination of Butter Adulteration

Havva Tumay Temiz<sup>\*A</sup>, Banu Sezer<sup>A</sup>, Aysel Berkkan<sup>B</sup>, Ismail Hakki Boyaci<sup>A</sup>

<sup>A</sup>Department of Food Engineering, Faculty of Engineering, Hacettepe University, 06800 Ankara, Turkey; <sup>B</sup>Analytical Chemistry Division, Faculty of Pharmacy, Gazi University, 06330, Ankara, Turkey.

\*ttemiz@hacettepe.edu.tr

**ABSTRACT:** Butter is an expensive milk fat product, which has been frequently exposed to adulteration practices through the addition of animal fats or other low-priced vegetable oils. In order to prevent these practices, Codex Standard 279-1971 requires the ratio of milk fat in butter at least 82% and the official method described in Regulation (EC) No 273/2008 requires the analysis of triacylglycerols by using gas chromatography (GC) as the reference method [1]. Due to the drawbacks of GC such as being time-consuming and requiring experienced personnel, rapid and simple alternative methods are needed for the determination of butter adulteration. Within this context, usage of spectroscopic methods namely Raman, fluorescence, Fourier Transform Infrared and attenuated total reflectance-mid-infrared have been reported in the literature [2-5]. Unlike from the reported studies, the potential of laser induced breakdown spectroscopy (LIBS) for determining butter adulteration with margarine was investigated in the present study. Differences in the mineral composition of butter and margarine samples have been taken into consideration. Inductively coupled plasma mass spectroscopy (ICP-MS) and atomic absorption spectroscopy (AAS) have been mainly used in literature to reveal the differences in mineral composition of these samples. However, the obligation for the mineralization of the samples constitutes the major disadvantage of these techniques. A high-energy laser pulse is used to ablate a small amount of sample in LIBS technique. A plasma that contains the mixture of excited neutral and charged atomic and molecular species is formed subsequent to the laser ablation. Since the light emissions from these species are measured when they return to the ground state, one is able to perform a multi-elemental analysis by using this technique [6]. In this study, LIBS spectra within the range of 186-900 nm were obtained for butter and margarine samples. Principal component analysis (PCA) and partial least squares (PLS) were applied on the collected LIBS data. A clear discrimination was observed by using principle component 1 and principle component 2, which explains 88.67% and 98.45% of the cumulative variance. PLS calibration and validation graphs were established with acceptable root mean square error of calibration (RMSEC=1.08) and validation (RMSEP=3.37) values. Relative standard error and relative error of prediction values were 12.2% and 11.1% while limit of detection (LOD) and limit of quantitation (LOQ) values were calculated as 3.9% and 11.8%. ICP-MS and AAS methods were both used as the reference methods of elemental analysis.

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## Identification of the Region of Cultivation of Ethiopian Coffee Using Spectrometric Data

Bewketu Mehari<sup>A</sup>, Mesfin Redi-Abshiro<sup>B</sup>, Bhagwan Singh Chandravanshi<sup>B</sup>, Sandra Combrinck<sup>A</sup>, Rob McCrindle<sup>\*A</sup>

<sup>A</sup>Department of Chemistry, Tshwane University of Technology, P/B X680, Pretoria 0001, South Africa; <sup>B</sup>Department of Chemistry, College of Natural Sciences, Addis Ababa University, Addis Ababa, Ethiopia.

\*rob.mccrindle@tut.ac.za

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*ABSTRACT: Coffee is one of Ethiopia's main sources of income, that country being the largest producer and exporter of Arabica coffee in Africa. Six varieties, Harar, Jimma, Kaffa, Wollega, Sidama and Yirgacheffe are grown in the east, west and south of the country. The commercial value of the crop is determined by the taste, which is dependent on the variety. Currently, the market relies on paper-traceability and is hence susceptible to fraudulent activities, both by the producers and purchasers of the coffee. An analytical method would assist in identifying the origin of the beans. An inductively coupled plasma-optical emission spectrometer was used to determine the concentrations of Ba, Ca, Cu, Fe, K, Mg, Mn, P, S and Si in beans collected from the regions. Principal component analysis was used to explore the natural groupings of the samples based on their elemental concentrations. Linear discriminant analysis provided classification models with an accuracy of 92% for the region of production and 79% for the variety. The elements that were most discriminating were Cu, Fe, Mn, P and S. The results indicate that initial screening using spectrometric analysis could serve to characterize the product and identify fraudulently labeled coffee with verification by the existing paper-based traceability system and sensory evaluation.*

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## Barcoding Approach for Determination of Vegetable Oil by Raman Spectroscopy.

Serap Durakli Velioglu<sup>A</sup>, Elif Ercioglu\*<sup>B</sup>, Havva Tümay Temiz<sup>B</sup>, Hasan Murat Velioglu<sup>C</sup>, Ali Topcu<sup>B</sup>, İsmail Hakki Boyacı<sup>B</sup>

<sup>A</sup>Department of Food Engineering, Faculty of Agriculture, Namik Kemal University, 59030 Tekirdag, Turkey;

<sup>B</sup>Department of Food Engineering, Faculty of Engineering, Hacettepe University, Beytepe 06800, Ankara, Turkey; <sup>C</sup>Department of Agricultural Biotechnology, Faculty of Agriculture, Namik Kemal University, 59030 Tekirdag, Turkey.

\*elifercioglu@hacettepe.edu.tr

**ABSTRACT:** In this study, edible oil samples from seven different vegetable oil sources (sunflower, corn, olive, canola, mustard, soybean and palm) were analyzed via Raman spectroscopy. This technique enabled the visual discrimination of different vegetable oils via their unique barcode figures. Visible differences were supported with chemometric analysis. For this purpose, principal component analysis was applied for the classification of set of samples by their level of differences arising from their barcode data. In addition, barcodes generated based on the Raman spectral data of seven vegetable oils were used for the determination of the eight fatty acids (palmitic (16:0), stearic (18:0), oleic (18:1n-9), linoleic (18:2n-6),  $\alpha$ -linolenic (18:3n-3), cis 11 eicosenoic (20:1n-9), erucic (22:1n-9) and nervonic (24:1n-9)) with R<sup>2</sup> values in the range of 0.989 - 0.970. Chemometric analysis, namely, principal component analysis (PCA) and partial least square (PLS) methods were used for data analysis. PCA was applied for discrimination of the samples according to the differences in their levels arising from their barcode data. A successful differentiation, based on second derivative barcodes of Raman spectra (2D-BRS) of vegetable oils was obtained. In addition, PLS method was applied on 2D-BRS in order to determine the major fatty acid (FA) composition of these samples. Coefficient of determination values for 16:0, 18:0, 18:1n-9, 18:2n-6, 18:3n-3, 20:1n-9, 22:1n-9 and 24:1n-9 were in the range of 0.970-0.989. Limit of detection (LOD) and limit of quantification (LOQ) values were found to be satisfactory (0.09–8.09 % and 0.30–26.95 % in oil) for these FAs. Advantages of both chemometric analysis and spectral barcoding approach have been utilized in the present study. Taking the second derivative of the Raman spectra has minimized background variability and sensitivity to intensity fluctuations. Spectral conversion to the barcodes has further increased the quality of information obtained from Raman spectra and also gave us a possibility to improve the visualization of the data. An optimization study has been performed in order to analyze the effect of different threshold values on the success of the developed method. Threshold value was optimized as %1 of the maximum absolute value of the second derivative and values lower than this threshold have been neglected in order to prevent the negative effects of these low intensity information on the spectral data analysis. As a result, applicability of spectral barcoding approach on Raman spectral data of vegetable oils has been presented with the present study. Converting Raman spectra of oils into barcodes, device readable representation of data, enables simpler presentation of the valuable information, and still allows further analysis such as classification of vegetable oils and prediction of their major FAs with high accuracy.

## Wine Analysis by ICPMS-2030

Uwe Oppermann\*

Shimadzu Europa GmbH, Analytical BU, 47269 Duisburg, Germany

\*uo@shimadzu.eu

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*ABSTRACT: Strict and steady control from the origin of the food to the final product is needed to protect customers against undesired contaminations and guarantee a high level of quality.*

*For simultaneous quantitative determination of the inorganic elements in wine, ICP-MS is the most preferable tool for quality control because of a high sensitivity (trace detection), a wide dynamic range and a high sample throughput. The Shimadzu ICPMS-2030 constitutes an easy and fast system to meet these requirements. Focal point in this market will certainly be the simultaneous evaluation of nutritional elements present in high concentrations (Na, K, Ca, Mg...), in combination with the evaluation of trace elements and toxic elements in very low concentrations (Pb, Cd, As, Hg, Th, Se...).*

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## Study of olive fruit ripening process by means of principal component analysis of hyperspectral FTIR images

González-Cabrera, M.\* , Domínguez-Vidal, A., Ayora-Cañada, M.J.

Department of Physical and Analytical Chemistry, Universidad de Jaén, Campus Las Lagunillas, s/n, 23071, Jaén, Spain; [adovidal@ujaen.es](mailto:adovidal@ujaen.es); [mjayora@ujaen.es](mailto:mjayora@ujaen.es);

\*[mgcabrer@ujaen.es](mailto:mgcabrer@ujaen.es)

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### ABSTRACT:

*Infrared spectroscopy is one of the most useful analytical tools for the exploration and characterization of bio-chemical properties and components of plants. The purpose of the present work is the study and evaluation of the information contained in a hyperspectral image of the olive fruit. By using mid-infrared microspectroscopy, it is possible to build a hyperspectral image through the collection of spectral data from a sample with spatial resolution. Analysing the results of the collected spectra, they can be mapped in two dimensions to produce an image of the spatial distribution of chemical components across a sample. In our case, the procedure consists in recording FT-IR spectra along a fresh and properly cut and prepared area of the sample, olive fruit. Samples of olive fruit were collected during the ripening process which include seventeen weeks.*

*We have been exploring different treatments of hyperspectral data, specially focusing on either univariate and multivariate procedures. The univariate analysis can be useful to observe the distribution of a single band of the IR spectra in the selected visible image, through the use of false-colour distribution maps. Moreover, a more advanced treatment can be performed with the intensities ratio of several infrared bands. But the most relevant methods to obtain bio-chemical information about the samples are the multivariate ones, because the univariate procedures can miss information of the entire range of the spectrum and the distortion effects between bands can always exist. Thus, we are working on the use of the principal component analysis (PCA) to a better understanding and discrimination of the olive tissues and to monitor bio-chemical changes taking place into the ripening process.*

*The FTIR hyperspectral images obtained using the classic method have allowed us to distinguish characteristic IR bands for both epicarp and mesocarp. Also, the phenomenon of olive oil accumulation in flesh vacuoles can be observed through the use of the intensities ratio between bands at  $1742\text{ cm}^{-1}$  and  $1687\text{ cm}^{-1}$ . Using the multivariate data analysis, it has been possible to reduce the number of variables, but preserving the most relevant information. It also can allow us to look for components that can be distributed differently in the samples and can contain different spectral contributions.*

*Having examined the loadings of the principal components, there are some spectral contributions helping to distinguish between olive tissues, as  $1713\text{ cm}^{-1}$  and  $1515\text{ cm}^{-1}$ , related to the C=O-H group of cutin esters and aromatic compounds, respectively. In the loading graphs, it is also remarkable the relation existing between certain bands of the IR spectrum. In conclusion, this work shows the potential of the treatment of FTIR hyperspectral images when interpreting chemical processes in tissue samples.*

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**Acknowledgments:** To the research group FQM-363 of the Universidad de Jaén.

## Arsenic Speciation and Cadmium Determination in Tobacco Leaves and Smoke

Koichi Chiba<sup>\*A</sup>, Takahiro Iwai<sup>A</sup>, Tomohiro Narukawa<sup>B</sup>

<sup>A</sup> Department of Environmental and Applied Chemistry, School of Science and Technology,  
Kwansei Gakuin University, 2-1 Gakuen, Sanda, Hyogo, 669-1337, Japan;

<sup>B</sup> National Metrology Institute of Japan (NMIJ), National Institute of Advanced Industrial Science and  
Technology (AIST), Tsukuba Central 3, 1-1-1 Umezono, Tsukuba, Ibaraki, 305-8563, Japan.

\*kk-chiba@kwansei.ac.jp

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**ABSTRACT:** The concentrations of arsenic (As) and cadmium (Cd) in the tobacco leaves, ash and smoke of 10 kinds of cigarettes collected from different countries worldwide were determined by ICP-MS after microwave-assisted digestion. Total As and Cd concentrations in the tobacco leaves ranged from 0.20 mg kg<sup>-1</sup> to 0.63 mg kg<sup>-1</sup> and 1.8 mg kg<sup>-1</sup> to 9.9 mg kg<sup>-1</sup>, respectively. By the speciation analysis of As in tobacco leaves and ash by HPLC-ICP-MS following acid extraction, arsenite [As(III)] and arsenate [As(V)] were determined and trace amount of monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), trimethylarsine oxide (TMAO), tetramethylarsonium (TeMA) and some unidentified As species were also found. Arsenic speciation for the smoke absorbed in an aqueous solution was carried out. The sum of As species in tobacco leaves, ash and smoke was in good agreement with the result of total As determination in each sample, and the recoveries of speciation were 100 ± 10 %. The distributions and the behaviors of As species were clarified.

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## High quality analysis of food by multivariate ToF-SIMS approach

Marco Consumi\*; Gemma Leone; Gabriella Tamasi; Claudia Bonechi; Claudio Rossi; Agnese Magnani.

Dipartimento di Biotecnologie, Chimica e Farmacia, University of Siena, Via A. Moro, 2 - 53100 Siena, Italy

INSTM-Siena UdR, Via G. Giusti, 9 – 50121 Firenze, Italy

CSGI-Siena UdR, Via della Lastruccia, 3 – 50019 Sesto Fiorentino (FI), Italy

\*marco.consumi@unisi.it

**ABSTRACT:** Nowadays there is a growing interest of researchers for the application of sophisticated analytical techniques in conjunction with statistical data analysis methods to the characterization of natural products to assure their authenticity and quality and to allow direct analysis of food to obtain maximum information. In this work, time-of-flight secondary ion mass spectrometry (ToF-SIMS) in conjunction with principal components analysis (PCA) are applied to study the chemical composition and variability of different food matrices:

- Sardinian myrtle (*Myrtus communis* L.): both berries alcoholic extracts and berries epicarps were analyzed. ToF-SIMS spectra show that the epicuticular waxes consist mainly of carboxylic acids with chain length ranging from C20 to C30, or identical species, formed from fragmentation of long-chain esters. PCA of ToF-SIMS data from myrtle berries epicarp distinguishes two groups characterized by a different surface concentration of triacontanoic acid. Variability in antocyanins, flavonols,  $\alpha$ -tocopherol, and myrtucommulone contents is showed by ToF-SIMS PCA analysis of myrtle berries alcoholic extracts.

- Seggianese olives and olive oil: three different groups of Seggianese olives: (i) treated with an insecticide (dimethoate) and a fungicide (copper oxychloride) (TU); (ii) untreated (UT); and (iii) treated-washed (TW) have been analyzed by ToF-SIMS. Intact olive slices and olive oil were analyzed. Principal component analysis (PCA) of the ToF-SIMS spectra were used to investigate differences/similarities among samples. Results showed that TW olives were more similar to UT samples than to TU samples. However, the washing process was not totally effective, since the treatment was able to induce alterations in the composition of the olives.

- Peaches and nectarine: samples of yellow-fleshed peaches (*Prunus persica* L. Batsch) and yellow-flesh nectarines (*Prunus persica* L. Batsch, var. *Nectarina*) of four different cultivars (RomeStar, ZeeLady, peaches; Venus, Nectaross, nectarines) from two geographic areas of Southern Italy, "Piana di Sibari" and "Piana di Metaponto", located on the Ionian coast of Calabria and Basilicata regions were analyzed. ToF-SIMS analysis confirmed the presence of Cyanidin and Phosphatidylcholine in the skin of peaches and nectarines, and Cyanidin, Phosphatidylcholine, Oleic Acid and Coniferyl Alcohol in the skin of seed. The Cluster analysis obtained from the skins of the seeds, constitutes a viable option for the geographical characterization of peaches and nectarines.

ToF-SIMS conjugated with statistical data analysis is a promising method for thoroughly investigating the chemical composition and variability of food and natural products, allowing to extrapolate information on geographical origin and possible adulteration.

# *Food Analysis Session*

## ***Food Analysis III***

(Mon. 12<sup>th</sup> of June, h. 14.45-16.00)

## Developing the Rolling Circle Amplification (RCA) Based Surface-Enhanced Raman Spectroscopy (SERS) Method for Genetically Modified Organisms (GMOs)

Burcu Guven<sup>\*A</sup>, Esra Acar Soykut<sup>B</sup>, Ismail Hakki Boyaci<sup>A</sup>, Ugur Tamer<sup>C</sup>

<sup>A</sup>Department of Food Engineering, University of Hacettepe, Ankara, Turkey; <sup>B</sup>Food Research Center, University of Hacettepe, Ankara, Turkey; <sup>C</sup>Department of Analytical Chemistry, University of Gazi, Ankara, Turkey.

\*burcuguven@hacettepe.edu.tr

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**ABSTRACT:** Within the scope of this study, a novel sandwich method based on rolling circle amplification (RCA) and surface enhanced Raman spectroscopy (SERS) have been developed as an alternative to polymerase chain reaction (PCR) for a rapid, sensitive and selective analysis of genetically modified organism (GDO). In this regard, gold (Au) surface, Au nanoparticles were used. After the optimization of nanoparticle surface modification and RCA parameters, an oligonucleotide probe which is specific to target sequence (35S DNA promoter) was immobilized onto the Au slide, and RCA reaction was performed successfully. A self-assembled monolayer was formed on Au nanoparticles by using 5,5'-dithiobis (2-nitrobenzoic acid) (DTNB), and the second probe of the 35S DNA promoter was immobilized on the activated Au slide surfaces. Quantification of the target sequence concentrations was performed via SERS spectra of DTNB on the Au nanoparticles. SERS spectra of target molecules were enhanced with the RCA reaction, and the detection limit was found to be 6.3 fM. The sensitivity of the developed RCA-SERS method was compared with the traditional method, and the detection limit was found to be 0.1 pM. Efficiency of the developed RCA-SERS method was analyzed in real system by amplifying the 35S promoter of Bt-176 maize gene with PCR. The results has shown that the developed RCA-SERS sandwich assay method is quite sensitive, selective and specific for target sequences in model and real systems.

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## Selenocysteine and selenium nanoparticle determination in selenium-rich yeast by coupled techniques and single particle ICP MS.

Katarzyna Bierla\*, Javier Jimenez-Lamana, Joanna Szpunar, Ryszard Lobinski

CNRS, Institut des Sciences Analytiques et de Physico-chimie pour l'Environnement et les Matériaux, IPREM UMR 5254, Hélioparc, 2, av. Pr. Angot, 64053 Pau, France.

\*katarzyna.bierla@univ.pau.fr

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*ABSTRACT: Selenium is an essential micronutrient playing a vital role in many biochemical and physiological processes. The deficiency of selenium is a world-wide problem which is addressed by supplementation. Selenium-enriched yeast is a popular food supplement and an established ingredient of Se-enriched premixes and finished feed products. The understanding and optimization of the biochemical processes of Se incorporation during yeast growth and the characterization of the final products requested by regulatory agencies require the development of suitable methods for speciation analysis.*

*Most of the methodological developments concerning the analysis of selenized yeast have been focused on the quantitative determination of selenomethionine (SeMet). Selenocysteine was hardly considered because of the absence of the selenocysteine insertion codon (UGA). These efforts culminated at the issue of a certified reference material (SELM-1) and resulted in the acceptance of the SeMet content as an indispensable parameter of the quality control of marketed yeast products. The other mainstream of analytical chemistry developments included the identification of the myriad of selenium metabolites allowing the quasi-complete characterization of the water soluble part of the Se yeast metabolome. To date, the mass balance of the determined selenium species has been showing the existence of "missing" selenium, species that could not be properly identified and determined.*

*The goal of the research was to find in which form these unaccounted for selenium species are present and to quantify them. We demonstrated unambiguously that despite of absence of UGA codon selenocysteine (SeCys) can be produced by yeast. The contribution discusses a systematic development of an analytical method for quantification of selenocysteine in Se-rich yeast. It is complemented by a study of the reactivity of Se-species during derivatization by carbamidomethylation. It was carried out by electrospray MS2 after purpose-designed 2D HPLC purification using ICP MS monitoring. The developed procedure allowed us to account for a missing fraction of ca. 15% of Se in the yeast sample.*

*The investigation of the remaining fraction demonstrated the presence of Se nanoparticles. Consequently, we developed an extraction procedure followed by their determination by single-particle ICP MS method for an acquisition in a single particle (SP) mode.*

*Examples of comprehensive speciation analysis of yeast samples accounting for the totality of selenium will be given.*

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## Application of Solid Sampling for the Determination of Total Fluorine in Some Fish Varieties and Other Seafoods by High-Resolution Continuum Source Graphite Furnace Molecular Absorption Spectrometry

Nil Ozbek<sup>A\*</sup>, Suleyman Akman<sup>A</sup>

<sup>A</sup> Department of Chemistry, Istanbul Technical University, Maslak, Istanbul, Turkey.

\*nil.ozbek@itu.edu.tr

**ABSTRACT:** Fluorine is the most abundant halogen and the thirteenth most common element in Earth's crust. Fluorine prevents the cavities and improves the oral and bone health whereas excessive fluoride consumption may cause dental and skeletal fluorosis, lead to increased likelihood of bone fractures, and oxidative stress in the liver. The main sources of fluoride that have been associated with increased dental fluorosis are fluoridated water, fluoridated supplements, foods and fluoridated dentifrices. Fluorine compounds, organic or inorganic, are commonly used in productions of pharmaceuticals, polymers, pesticides, surfactants, refrigerants while added to toothpastes and drinking waters. Therefore, it can be expected that free fluoride ions or covalently bound organic and biological fluorine compounds released to aquatic environment from various sources due its commonly uses in many products. In addition, from combustion of coal, fluorine released to atmosphere and its transfer to aquatic environment may be expected. As a result, fluorine concentrations in fish samples should need great attention. High-resolution continuum source AAS (HR-CS AAS) provides a very high resolution so that it is possible to isolate a very narrow wavelength overlapping exactly with the center of the analytical line of the molecule. Moreover, since the three dimensional wavelength-time resolved absorption spectrum in the near vicinity of the analyte line can be visualized, the spectral interferences originated from matrix components formed in the graphite furnace can be controlled. Due to its unique properties, HR-CS AAS is an appropriate instrument to determine non-metals. Fluorine has been determined via molecular absorption of CaF, BaF, GaF, AlF, SrF formed in flame or graphite furnace of HR-CS AAS using solution and solid sampling techniques. In this study, total fluorine concentrations in some fish species as well as mussels, squids (calamary) and shrimps were determined by means of molecular absorption of calcium monofluoride generated in a graphite furnace using high resolution continuum source atomic absorption spectrometer and direct solid sampling technique. The fish fillets and other seafoods were dried at 110 °C, minced finely, put on the platform below 1 mg and introduced to the graphite furnace together with 20 µg of calcium by means of a solid sampler. The effects of CaF wavelength, graphite furnace program, amount of sample introduced to the furnace, the use of modifier as well as coating the graphite tube with a permanent modifier on the determination of fluorine were investigated and optimized. Fluorine was determined at 606.440 nm via molecular absorption of CaF applying a pyrolysis temperature of 1000 °C and a molecule forming temperature of 2200 °C using aqueous F standards for calibration. The absolute limit of detection and characteristic mass of the method were 0.18 ng and 0.14 ng of fluorine, respectively. The fluorine in a CRM and the spikes added to some solid fish portions were satisfactorily recovered. By applying the optimized parameters, the concentrations of fluorine in various fish species and seafoods were determined. Finally, micro-scale distributions of fluorine in fish samples were determined.

## Near infrared spectroscopy and X-ray fluorescence data fusion for olive nutritional status determination.

Francisco Comino <sup>\*A</sup>, Ana Domínguez-Vidal <sup>A</sup>, María José Ayora-Cañada <sup>A</sup>, Víctor Aranda Sanjuán <sup>B</sup>

<sup>A</sup> Department of Physical and Analytical Chemistry, Universidad de Jaén, Campus Las Lagunillas S/N, 23071 Jaén, Spain. [adovidal@ujaen.es](mailto:adovidal@ujaen.es); [mjayora@ujaen.es](mailto:mjayora@ujaen.es); <sup>B</sup> Department of Geology, Universidad de Jaén, Campus Las Lagunillas S/N, 23071 Jaén, Spain. [varanda@ujaen.es](mailto:varanda@ujaen.es)

[\\*fcomino@ujaen.es](mailto:fcomino@ujaen.es)

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**ABSTRACT:** Olive cultivation and olive oil production are a worldwide important business, typically concentrated in the Mediterranean countries. Olive growing has become more intensive over the last three decades, and is using an increasing amount of agricultural land and resources. To maximize olive production with the minimum environmental cost, it is necessary to realize a correct fertilisation, since there is an optimal level of nutrients for maximum yield while excessive fertilisation has negative environmental effects. Suitable fertilisation decisions require characterization of plant nutritional status. Currently, this is carried out by chemical analyses of leaf samples performed in the laboratory. These analyses normally include long and tedious samples preparation, and further measure by titration, inductively coupled plasma (ICP), and atomic absorption spectroscopy (AA) among others. Because these methods are expensive and time consuming, especially when working with high amount of samples, the situation calls for the introduction of an efficient measurement method that can effectively replace the traditional laboratory routine analysis. In this way, spectroscopic techniques with no sample preparation emerge as an alternative that can provide similar results than laboratory techniques for plant macro and micronutrients measurement. Fourier Transform Near Infrared Spectroscopy (FT-NIR) and X-Ray Fluorescence (XRF) was applied to olive leaf samples, with light sample preparation (only oven dried and grounded), in order to determine their content in N, P, K, Ca, Mg, Mn, Zn and B, principal nutrients for olive. Predictive models were constructed using Partial Least Squares Regression (PLSR) technique for FT-NIR and XRF separately, obtaining unequal models for nutrients. The aim of present study was try to investigate the combination of these two spectroscopic techniques combine with chemometrics, using different data fusion levels in order to get more robust and accurate predictive models, comparing performance of different data fusion levels. Low-level data fusion, which consist in a fusion or concatenation of both raw data, lightly improve some predictive models like Ca, Mn and B, but get some poorer models for some nutrients like N, cause XRF is not as sensitive as FT-NIR to organic phase and direct fusion of data prove not to be the best option. Mid-level data fusion consists in a previous variable selection or transformation using chemometrics, like principal component analysis, and using these fused variables for the construction of predictive models. In our case mid-level data fusion was performed over the scores obtained from PCA of both FT-NIR and XRF, and predictive models obtained using PLSR get better prediction results for Mn, Zn, B and especially for P, being the other models similar to the obtained without fusing data. This demonstrates that data fusion of FT-NIR and XRF could be a good alternative to determine olive nutritional status.

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## Nutritional characterization by laser-induced breakdown spectroscopy of healthy and *Aphelenchoides* sp. infected soybean leaves.

Anielle C. Ranulfi <sup>\*A,B</sup>, Giorgio S. Senesi <sup>D</sup>, Jonas B. Caetano <sup>A,C</sup>, Maurício C. Meyer <sup>E</sup>, Aida B. Magalhães <sup>A</sup>, Paulino R. Villas-Boas <sup>A</sup>, Débora M. B. P. Milori <sup>A</sup>

<sup>A</sup>Embrapa Instrumentation, PO Box 741, 13561-206, São Carlos, SP, Brazil; <sup>B</sup>São Carlos Institute of Physics, University of São Paulo, PO Box 369, 13560-970, São Carlos, SP, Brazil; <sup>C</sup>Physics Department, Federal University of São Carlos, 13365-905, São Carlos, SP, Brazil; <sup>D</sup>CNR, Istituto di Nanotecnologia (NANOTEC) – PLASMI Lab, Bari, 70126 Bari, Italy; <sup>E</sup>Embrapa Soybean, PO Box 231, 86001-970, Londrina, PR, Brazil.

\*anielle.ranulfi@usp.br

**ABSTRACT:** Soybean and its derivatives are one of the most valuable and traded agricultural commodities worldwide. The major problem faced by the producers which threatens the yield of soybean, is associated to diseases. In Brazil, the green stem and foliar retention (GSFR) disease was recently described as affecting soybean plants, for which no effective method of early diagnosis and treatment is known. In an attempt to investigate plant changes caused by GSFR infection, pelletized leaves from healthy and sick soybean plants of two varieties from two different places of Brazil were evaluated comparatively by laser-induced breakdown spectroscopy (LIBS) for their content of the three macro nutrients Ca, K and Mg. Atomic Absorption Spectrometry (AAS) was used as the reference technique. The relative simplicity of LIBS instrumentation and the minimal sample preparation required makes it a valuable tool to be applied to the nutritional investigation and disease diagnosis of plants. The Pearson coefficients obtained for the correlation between LIBS and AAS data were close to 0.80 for the three nutrients analyzed, which can be considered good for the complex biological matrix analyzed. The Student t-test was applied separately to the normalized broadband spectra of healthy and infected leaves of the two soybean varieties by comparing the spectra intensity in order to explore the spectral ranges that present the most significant differences for Ca, K and Mg peaks, so reducing the spectral data and the computational cost of analysis. Results obtained by principal component analysis (PCA) applied to reduced data allowed to discern between healthy and infected plant leaves with 84% of variance retained by the two first principal components. In particular, the PCA loading of the specific ranges selected by the statistical test and the PCA score-plot of principal components 1 and 2, showed that a higher Ca and Mg content in leaves was related to healthy soybean leaves, whereas a higher K content could be related to the development of the GSFR disease. Further, these findings were in good agreement with the corresponding results obtained by the AAS reference technique. LIBS data analyzed by classification via regression (CVR) associated with partial least square regression (PLSR) yielded success rates higher than 80% in differentiating healthy and infected soybean leaves. The capacity of LIBS to discriminate between healthy and diseased soybean plants of two varieties thus confirms the robustness of the technique applied to complex biological matrices. This also in comparison to the conventional AAS technique, which can be high susceptible to errors, as it involves laboriously and time-consuming steps. In conclusion, this study demonstrates the possibility of using LIBS as a promising and convenient analytical GSFR diagnostic tool able to discern between healthy and GSFR-infected soybean plants by analyzing the three macronutrient Ca, K and Mg, thus contributing to find sustainable solutions to early control of this disease and protect the growth of soybean and the development of its production and yield.

# *Food Analysis Session*

## ***Food Analysis IV***

(Wed. 14<sup>th</sup> of June, h. 9.15-10.45)

## Comparison of Laser Induced Breakdown Spectroscopy Analysis Between Milk and Milk Powder

Gonca Bilge<sup>\*A</sup>, Banu Sezer<sup>B</sup>, Ismail Hakki Boyaci<sup>B</sup>

<sup>A</sup>Nanosens A.Ş., 06790 Ankara, Turkey;

<sup>B</sup>Department of Food Engineering, Hacettepe University 06800 Ankara, Turkey.

\*goncabilge@nanosens.com.tr, sezerrbanu@gmail.com, ihb373@gmail.com

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**ABSTRACT:** Liquid analysis by LIBS is so complicated process due to difficulties with formation of plasma in liquid and collection of light. To avoid these, some approaches are performed such as aerosol formation and transforming of liquid to solid state. However, performance of LIBS in liquid samples is still controversial. In this study, a comparative study was performed to determine the performance of LIBS in liquid and solid phase samples. For this purpose, milk was chosen as model sample so milk powder as solid sample and milk as liquid sample were used in experiments. Different experimental setups have been constructed for each sampling technique. A rotary table was used for solid sampling technique to measure many regions of sample and an airbrush was used for liquid sampling technique to produce aerosol phase as commercially available systems. Then optimizations were performed to determine suitable parameters such as delay time, laser energy, repetition rate, speed of rotary table for solid sampling technique and flow rate of carrier gas for liquid sampling technique. The effect of parameters on signal to noise ratio (SNR) and relative standard deviations (RSD) were investigated. Target element was determined as Ca which is critically important element in milk for determining of nutritional value and determining of Ca addition. For data analysis standard calibration method and multivariate data analysis techniques were performed and compared with each other. Indicators of method performance values such as  $R^2$  and relative standard deviation (RSD) values were calculated. In optimum parameters limit of detection (LOD), limit of quantification (LOQ) and RSD values were calculated as 2.73%, 8.26% and 5.37% respectively for milk powders samples while LOD, LOQ and RSD values were calculated as 0.12%, 0.37%, and 6.10% for milk samples. It can be said that LIBS is applicable method in both liquid and solid samples with suitable systems and parameters. It was shown that applicability of simple systems for liquid analysis instead of expensive equipments. However, liquid analysis need more developed systems for more accurate results.

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## Quantitative prediction of coffee adulteration by defective beans using Laser-Induced Breakdown Spectroscopy

Tiago Varão Silva <sup>A</sup>, José Anchieta Gomes Neto <sup>A</sup>, Débora Marcondes Bastos Pereira Milori <sup>B</sup>, Ednaldo José Ferreira <sup>B</sup>, Edilene Cristina Ferreira\*<sup>A</sup>.

<sup>A</sup>Departamento Química Analítica, UNESP-AQA, Araraquara, São Paulo, Brasil.

<sup>B</sup>Embrapa Instrumentação, São Carlos, São Paulo, Brasil.

\*varao29@yahoo.com.br

**ABSTRACT:** Coffee is one of the most popular beverages around the world. Its economic value as well as drink quality features are strongly related to the presence of defective beans, specially those called Black, Green and Sour (BGS). Blends of the cited beans in coffee causes negative impacts on the beverage quality. In order to aggregate value and expand internal consumption, the Secretary of Agriculture of São Paulo/Brazil, established the maximum contents of BGS defects in different coffee classes: for Gourmet (0%), Superior (up to 10%) and Traditional (up to 20%). Despite norms, quality is still assessed by a panel of expert tasters by using a subjective, costly and slow analysis. Thus, a simple, fast, low-cost and reliable analytical method is important for coffee quality control for a highly standardized, competitive and modern coffee industry. Laser-Induced Breakdown Spectroscopy (LIBS) stands out as a promising technique since it does not require (or requires minimum) sample preparation, allowing a simple, fast and multielemental analysis. The aim of this reported study was to develop a LIBS-based method for detection of coffee adulteration related to the mixes of BGS. For this purpose, unroasted good and BGS beans were individually milled using a cryogenic mill. Masses of good and defective beans were mixed to produce calibration and test sets. For the calibration set, BGSs were mixed with the good beans sample to produce standards of: 0, 3, 6, 9, 12, 15, 18, 21, 24, 27 and 30% of BGS. For the validation set, the produced samples contained: 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26 and 28% of BGS. The mixtures were homogenized using a mortar and a pistil and converted into pellets by the application of 10 tons of pressure. This procedure was repeated in order to obtain five pellets for each mixing conditions. Then, the pellets were carried to LIBS analysis and 40 laser pulses were applied for each pellet. The obtained spectra were preprocessed by using Standard Normal Variate (SNV) to minimize natural measurements fluctuations and 1st derivative. Spectral ranges firstly considered were that corresponding to emission lines of C, H, N and O, which are elements predominantly present in organic compounds: C (191,8- 195,3nm), N (741,7 - 743,57nm), N (743.67- 746.0 nm), N (746.0 - 749.0 nm), C<sub>2</sub> (515.3-517.1 nm), CN (384.6-389.9 nm), H (625.9-685.8 nm) and O (773.6 - 782.5 nm). Relevant variables were selected by using highest linear correlation between the percentage of defective BGS and variation rates (maximum and minimum) of mentioned lines. Variables showing correlation coefficients higher than 0.6 were selected for building calibration models: maximum of C(I) 193.0 nm, minimum for the N(I) lines (742.3 nm and 746.8 nm) and Oxygen (I) (777.4 nm). Using these variables a linear multivariate calibration model was built. The model showed *r* and Root Mean Squared Error Calibration (RMSEC) of 0.95 and 2.5%, respectively. For the prediction of the validation samples, *r* = 0.95 and RMSEV = 2,8%. These results shows the potential of LIBS to be used in coffee industry for quality control. The proposed method is simple fast and robust for evaluated conditions.

**Acknowledgements:** Consórcio Pesquisa Café, FAPESP e CAPES



## Food analysis by Laser Induced Breakdown Spectroscopy (LIBS)

J.O. Caceres<sup>A</sup>, S. Manzoor<sup>A</sup>, S. Moncayo<sup>A,B</sup>, D. Rosales<sup>A</sup>, R. Izquierdo-Hornillos<sup>A</sup>, J. Anzano<sup>C</sup>

<sup>A</sup>Department of Analytical Chemistry, Faculty of Chemistry. Complutense University. 28040 Madrid, Spain; <sup>B</sup>Institut Lumière Matière, UMR5306 Université Lyon 1-CNRS, Université de Lyon 69622 Villeurbanne cedex, France ; <sup>C</sup>Laser Laboratory, Dept. of Analytical Chemistry, Faculty of Sciences, University of Zaragoza, P. Cerbuna, 50009-Zaragoza, Spain

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**ABSTRACT:** Our research group has been working on exploring the analytical applications of Laser Induced Breakdown Spectroscopy (LIBS). During the last years, a very significant part of it has been dedicated to applying LIBS for the development of methodologies for the traceability, adulteration and quality assurance of food. Successful results have been achieved in the analysis of wines in order to preserve the Protected Denomination of Origin (PDO), adulteration in honey, olive oils and milk<sup>1,2</sup>. As all these samples have a different nature and laser-matter interaction, thus in each case a separate protocol for LIBS measurements and sample preparation was designed. A very important part of this research is the development and progress made in the data analysis, applying a wide range of chemometric methods and evaluating the essential parameters needed to be considered for a classification process<sup>3</sup>. Therefore, this work includes a review of all these studies presenting the procedure from sample preparation to LIBS measurements and data analysis, along with important results obtained. This will show the utility and progress of this technique made in the field of food analysis.

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## Determination of Cu, Fe, Mn and Zn in wheat flour using TXRF: Comparison with FAAS and ETAAS

Sebastián Mondutey<sup>A</sup>, Ignacio Machado<sup>B</sup>, Natalia Pastorino<sup>A</sup>, Valeria Arce<sup>A</sup>, Fiorella Iaquinta<sup>B</sup>,  
Mariela Pistón\*<sup>B</sup>

<sup>A</sup>Laboratorio de Bromatología de la Intendencia de Montevideo, Sector Análisis Elemental, Montevideo, Uruguay; <sup>B</sup>Grupo de Análisis de elementos Traza y desarrollo de estrategias simples para Preparación de Muestras (GATPREM), Analytical Chemistry, Faculty of Chemistry, Universidad de la República, Montevideo, Uruguay.

\*mpiston@fq.edu.uy

**ABSTRACT:** Total reflection X-ray fluorescence (TXRF) is a multi-elemental technique that meets the requirements for trace analysis of different kind of samples. One of the main advantages is the simplicity of the sample preparation procedure without digestion. Recent applications of TXRF in food analysis were reported showing that this technique offers a fast way to perform quantitative analysis with detection limits (LOD) comparable to other atomic techniques such as flame absorption atomic spectroscopy (FAAS), electrothermal absorption atomic spectroscopy (ETAAS) and inductive coupled plasma optical emission spectroscopy (ICP-OES) widely used for trace element analysis in food. Four essential trace elements present in wheat flour were determined using TXRF and the results were compared with those obtained performing classical analysis using FAAS (Fe, Zn) and ETAAS (Cu, Mn). For TXRF analysis wheat flour was sieved and 500 mg were suspended in 10 mL of HNO<sub>3</sub> 20 % (w/v) with Ga as internal standard (100 ng). 5 µL of each sample were deposited on a quartz sample carrier and dried on a hot plate at 60°C. The measurements were performed using a Bruker S2 Picofox equipped with Mo tube, operated at 50kV and 600 µA, and Silicon-Drift Detector. Each replicate was measured for 300 seconds. Quantitative analysis was performed by internal standard addition procedure. A microwave-assisted digestion was carried out for the determination of Cu and Mn by ETAAS and Fe and Zn by FAAS. 0.5 g of each sample were digested with 6 mL of HNO<sub>3</sub> (ramp for 15 minutes until power 600 W then hold for 15 minutes) after the digestion the volume was completed to 10 mL with ultrapure water. A certificate reference material (CRM-Wheat flour, NIST 1567a) and five commercial samples were analyzed. LOD using TXRF were 0.29 mg kg<sup>-1</sup>(Cu), 0.55 mg kg<sup>-1</sup>(Mn), 0.44 mg kg<sup>-1</sup>(Fe) and 0.27 mg kg<sup>-1</sup>(Zn). In the case of ETAAS, LOD were 0.014 mg kg<sup>-1</sup>(Cu) and 0.64 µg kg<sup>-1</sup>(Mn) while for FAAS where 0.20 mg kg<sup>-1</sup>(Fe) and 0.08 mg kg<sup>-1</sup>(Zn) using the 3s criteria. Recovery percentages for the CRM analysis ranged from 96 to 116 % for TXRF and from 97 to 109 % for ETAAS and FAAS for all the elements. Precision for TXRF depends critically on the particle size of the sample when the suspension was prepared. In optimum conditions the RSD % was less than 9 % for all the studied elements (n=6). For FAAS the RSD % was less than 7 % while for ETAAS was less than 9 % in all cases (n=6). Concentration levels of the four elements for the commercial samples differed in less than 12% between TXRF and FAAS or ETAAS. For this matrix LOD are significant lower for FAAS and ETAAS than for TXRF, but for Cu, Fe, Mn and Zn determination, TXRF is a suitable technique with accurate results and the advantages of the simple sample treatment procedure. For good precision particle size of the sample must be exhaustively optimized. TXRF is a promising technique for routine and screening analysis in foodstuff very fast and simple to perform and environmentally friendly. Acknowledgements: Comisión Sectorial de Investigación Científica (CSIC) and Agencia Nacional de Investigación e Innovación (ANII).

## Qualitative and quantitative analysis of milk for the detection of adulteration by Laser Induced Breakdown Spectroscopy.

S. Moncayo <sup>A</sup>, S. Manzoor\*<sup>A</sup>, J. D. Rosales<sup>A</sup>, R. Izquierdo<sup>A</sup>, J. Anzano <sup>B</sup>, J. O. Cacereso<sup>A</sup>

<sup>A</sup>Química Laser, Department of Analytical Chemistry, Faculty of Chemical Sciences, Complutense University, 28040 Madrid, Spain; <sup>B</sup>Department of Analytical Chemistry, Faculty of Sciences, University of Zaragoza, Pedro Cerbuna 12, 50009, Zaragoza, Spain

\*smanzoor@ucm.es

**ABSTRACT:** Milk due to its nutritional importance is among the most consumed food and has a great economic importance. Therefore, it is one of the main targets of adulteration, where mixing milk of different animal species, fat replacement and modification of the protein content by introducing an adulterant such as melamine ( $C_3H_6N_6$ ) are among the most common ones [1,2]. The addition of water has only economic and nutritional effects, however, the mixture of milk from different animal origin can produce adverse allergic reaction and the addition of melamine to increase the protein content causes serious health problems such as kidney disorder and even death of the consumer [3]. Furthermore, adulteration with melamine cannot be easily identified in routine analysis as the non-protein nitrogen detection by usual procedures for protein determination is not possible. Although there is a need in the food industry to improve quality and process controls, the application of LIBS technique in food control analysis has not been sufficiently explored and only few studies can be found in literature. The present work focuses on the development of a fast and cost effective method based on Laser Induced Breakdown Spectroscopy (LIBS) to the quality control, traceability and detection of adulteration in milk. Two adulteration cases have been studied; a qualitative analysis for the discrimination between different milk blends and quantification of melamine in adulterated toddler milk powder. Principal Component Analysis (PCA) and Neural Networks (NN) have been used to analyze LIBS spectra obtaining a correct classification rate of 98% with a 100% of robustness. For the quantification of melamine, CN emission band were used employing multivariate calibration NN model obtaining correlation coefficient ( $R^2$ ) values of 0.999. The results of the use of LIBS technique coupled with chemometric analysis are discussed in terms of its potential use in the food industry to perform the quality control of this dairy product.

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## Fast Detection of Adulteration in Honey using Laser-Induced Breakdown Spectroscopy and Neural Networks.

C. Rico, S. Manzoor, J.D. Rosales, J.O. Cáceres

Laser Chemistry Lab., Department of Analytical Chemistry, Faculty of Chemical Sciences, Complutense University, Avda. Complutense s/n, 28040, Madrid.

\*maririco@ucm.es

*The system of quality assurance to control fraud, preserve the Protected Denomination of Origin (PDO) and special characteristics of honey is regulated by law [1]. The amount and relative proportion of the mineral elements such as Mg, Ca, K and Na in honey depends on several factors such as flowering, flowers type, climate, water availability and quality, soil type and the way in which the honey is elaborated and stored [2,3]. Laser induced breakdown spectroscopy (LIBS) has been a subject of research for the past few decades because of its unique features and wide variety of applications in various fields. In recent years, LIBS has become a powerful analytical tool because of its ability to carry out a rapid qualitative and quantitative analysis of different samples [4]. LIBS analyzes a sample by direct measurement of the atomic emission of the elements from a laser-induced plasma generated by the ablation of the sample, providing an immediate spectral fingerprint that is representative of its elemental composition. Moreover, the technique requires little or no sample preparation. Although there is a loss of molecular information in plasma, this technique has provided excellent results for the identification of many polymer organic compounds, explosives, and bacteria. The intensities of C, H, N, and O lines and the C/H, C/O, and C/N intensity ratios have been used for the classification of organic compounds [5]. In this work, a quick and cost effective method based on Laser Induced Breakdown Spectroscopy (LIBS) and Neural Networks (NN) has been developed and applied to the identification of the quality control and PDO of honey. The samples analyzed belonged to the most important Spanish PDOs. Instant identification of the samples was achieved using a spectral library, which was obtained by analysis of representative samples using a single laser pulse and treatment by NN. The results obtained allowed the identification of the honey tested with a certainty of above 98%. Single-shot measurements were enough for clear identification of the samples.*

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# *Archeology & Cultural Heritage Session*

## ***Arch&Heritage I***

*(Mon. 12<sup>th</sup> of June, h. 9.45-10.45)*

## **In situ and remote spectroscopic characterization of Cultural Heritage surfaces**

Roberta Fantoni\*

ENEA – FSN-TECFIS C.R. Frascati, Via Enrico Fermi 45, 00044 Frascati, (Rome), Italy

\*roberta.fantoni@enea.it

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*ABSTRACT: Optical and spectroscopic techniques offer unique possibilities for non destructive or microdestructive characterization of painted Cultural Heritage surfaces. The development of fast laser scanners in combination with sensitive CCD detector gave the chance to design and operate portable systems suitable to in situ an remote spectroscopic imaging. At ENEA Frascati different prototypes have been developed and patented to collected reflectance and fluorescence images excited at different ultraviolet and visible laser wavelengths, Raman and LIBS signals. Portable integrated instruments suitable for operation at different distance from a 1.5 to 30 m, have been assembled and operated in laboratory on multi-layered samples and in field campaigns on CH painted surfaces. ILS (Integrated Laser System) prototype, realized for remote (LIBS/RAMAN/LIF) within the European EDEN project, LIRA (LIBS/Raman) and CALIFFO (LIF) compact low cost instruments, both realized within the COBRA regional project will be presented. Results will be shown for LIBS stratigraphy in comparison with other spectroscopic laboratory techniques, and for LIF/Raman results obtained on historical pigments and modern consolidants in Etruscan tombs and Roman catacombs.*

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## Multi-analytical approach for the evaluation of the stability of painting materials for conservation purposes.

Giorgia Agresti <sup>A</sup>, Giuseppe Bonifazi <sup>B</sup>, Giuseppe Capobianco <sup>B</sup>, Fabio Morresi <sup>C</sup>, Claudia Pelosi <sup>\*B</sup>,  
Sara Rossi <sup>A</sup>, Ulderico Santamaria <sup>A,C</sup>, Silvia Serranti <sup>B</sup>

<sup>A</sup> Laboratory of Diagnostics for Conservation and Restoration, University of Tuscia, Largo dell'Università, 01100 Viterbo, Italy, [agresti@unitus.it](mailto:agresti@unitus.it), [sara.myricae@gmail.com](mailto:sara.myricae@gmail.com), [santamaria@unitus.it](mailto:santamaria@unitus.it); <sup>B</sup> Department of Chemical Engineering Materials & Environment, Sapienza, Rome University, Via Eudossiana 18, 00184 Rome, Italy, [giuseppe.bonifazi@uniroma1.it](mailto:giuseppe.bonifazi@uniroma1.it), [giuseppe.capobianco@uniroma1](mailto:giuseppe.capobianco@uniroma1), [silvia.serranti@uniroma1.it](mailto:silvia.serranti@uniroma1.it); <sup>C</sup> Laboratory of Diagnostics for Conservation and Restoration, Vatican Museums, 001100 Vatican City, [fabio.morresi@gmail.com](mailto:fabio.morresi@gmail.com).

[\\*pelosi@unitus.it](mailto:*pelosi@unitus.it)

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**ABSTRACT:** The paint layers of art objects are daily subject to aggression by atmospheric agents that, with different mechanisms of degradation, can damage them irreparably. The main causes of alteration in artistic materials are climate, weather and biological agents. The degradation patterns occur also in commercial materials used for conservation and restoration, sometimes with unknown and unpredictable mechanisms. The evaluation of stability of commercial products, used in conservation, is so fundamental in assessing their possible use and for this several techniques can be applied. A lot of techniques, requiring micro-samples, cannot be used in conservation especially do to the difficulty or impossibility to repeat the measurements in the same points and during time. The aim of this contribution is to investigate the stability of a selected number of painting materials by different spectroscopic techniques and under different ageing conditions. The aim is also to evaluate the sensitivity of the chosen techniques in identifying the variations on paint layers, induced by photo-degradation, before they could be observed by eye; furthermore, the aim is also to use, by multivariate approach, the supervised classification methods for monitoring the painted surface changes. As painting materials, starting from previous studies, some commercial water colours, supplied by Winsor&Newton, and a conspicuous group of natural ochre and earths (whose origin is known and applied by Arabic gum as binder in order to have the same binder of commercial water colours) were selected in order to compare their stability. All pigments were characterized by different analytical techniques such as: X-ray fluorescence spectroscopy, Fourier transform infrared spectroscopy, X-ray diffraction, in order to know the composition of the chosen materials. These painting materials were applied on setting layers in order to create colour check tables with 54 different pigments, both organic and inorganic, for simulating the high variability on real artwork. One table was used as blank. The other two were aged under controlled UV irradiation. In particular one table was aged in Solar Box chamber under the following conditions: temperature 55 °C, irradiation power 550 W/m<sup>2</sup>, UV filter at 280 nm, relative humidity 50%. The other one was aged at ambient temperature under UV lamps Philips TUV36 operating at 36W, emission at 250 nm. Measurements were taken at 0, 196, 268 and 504 hours. Colour and chemical changes were investigated by reflectance spectrophotometry in the visible range through a X-Rite CA22 spectrophotometer and hyperspectral imaging (HSI), in particular in the SWIR range by Sisuchema XL (Specim®). The choice of these techniques allowed non-invasive and non-destructive control, exactly in the same points, of the variations in the painting samples before the changes could be observed by naked eyes. Data from colour measurements and HSI when compared at the same times of ageing.

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*Archeology & Cultural Heritage Session*  
***Arch&Heritage II***

*(Mon. 12<sup>th</sup> of June, h. 11.15-12.45)*

## Chemical changes in oil paints containing copper-based green pigments: a systematic investigation by ATR-FTIR spectroscopy.

Laura Cartechini<sup>\*A</sup>, David Buti<sup>B</sup>, Francesca Rosi<sup>A</sup>, Chiara Anselmi<sup>A</sup>, Sara Centurioni<sup>C</sup>, Fabio Talarico<sup>C</sup>, Gloria Tranquilli<sup>C</sup>, Carla Zaccheo<sup>C</sup>, Costanza Miliani<sup>A</sup>

<sup>A</sup>Istituto di Scienze e Tecnologie Molecolari, CNR, Via Elce di Sotto 8 Perugia, Italy; <sup>B</sup>CATS- SMK, Sølvgade 48-50, 1307 Copenhagen K, Denmark, <sup>C</sup>Istituto Superiore per la Conservazione ed il Restauro – ISCR, Roma, Italy

\*laura.cartechini@cnr.it

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**ABSTRACT:** In this research work ATR-FTIR spectroscopy was used for a systematic investigation of the chemical changes induced in oil paints by the presence of selected copper-based green pigments. This class of pigments, widely used in traditional oil painting, has deserved particular interest by restorers and conservation scientists since they play a primary role in the chemical decay of the paint organic matrix. The impact on the aesthetic value of precious artworks is significant, being darkening of the paint surface the most dramatic effect. In order to explore the reactivity of different copper-based green pigments, oil paint mock-ups with neutral verdigris, emerald green, chrysocolla and malachite were prepared and aged in conditions of controlled RH% (45% and 90%) and temperature (40°C). These pigments, indeed, have very different chemical nature, ranging from purely inorganic compounds to organo-metallic complexes, and thus present a variety of physical and chemical properties which strongly affect their reactivity. Chemical changes of the model oil paints have been monitored at fixed time intervals by ATR-FTIR and reflection FTIR spectroscopy. Spectral data show a remarkable reactivity for all the systems at the higher RH% condition, leading to an evident darkening of the paint surface combined with the formation of Cu-oxalates and carboxylates. Furthermore changes of pigment molecular structure were observed both for verdigris and emerald green. Complementary point and imaging analyses by micro-ATR-FTIR were performed on transversal sections of the aged paints in order to provide information on the distribution of the alteration products and possibly on the mechanism of formation. In order to support our experimental findings, spectroscopic analyses of micro-samples from a XVI century oil painting showing a darkening of the green areas made with a copper-based pigment were performed. The painting, dated 1573, belongs to the school of Tiziano and its recent restoration at ISCR offered the opportunity of investigating the severe alteration state of the green paint. Interestingly, comparing the results collected on the preserved green areas protected by the frame with those from the strongly darkened paint on the exposed surface, we found a confirmation for a pronounced presence of copper carboxylates and oxalates in the degraded paint. In this presentation an overview of the spectroscopic data obtained with different experimental FTIR spectroscopy configurations will be given and the results achieved for a significant variety of systems will be discussed attempting to provide a better understanding of this important alteration phenomenon affecting historical paintings. This work has been financially supported by the national research projects SICH (Project No. 2010329WPF\_001) founded by the Italian PRIN 2010-2011 program.

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## Rare Earth Elements analysis to identify anthropogenic signatures at the Valle del Serpis (Spain) Neolithic settlements

Gianni Gallelo<sup>\*ABC</sup>, Joan Bernabeu<sup>B</sup>, Agustin Diez<sup>B</sup>, Pilar Escriba<sup>B</sup>, Agustin Pastor<sup>C</sup>,

Marco Lezzerini<sup>D</sup>, Mark E Hodson<sup>E</sup>, Daryl Stump<sup>A</sup>

<sup>A</sup> Department of Archaeology University of York, King's Manor York YO17EP, UK; <sup>B</sup> Department of Prehistory, Archaeology and Ancient History University of Valencia, Avda. Blasco Ibáñez 28 Valencia 46010, Spain;

<sup>C</sup> Department of Analytical Chemistry University of Valencia, 50 Dr. Moliner Street, 46100 Burjassot, Valencia Spain; <sup>D</sup> Department of Earth Sciences, University of Pisa, Via S. Maria 53, 56126 Pisa, Italy; <sup>E</sup> Environment Department University of York, Wentworth Way Heslington York YO105NG, UK.

\*Gianni.gallelo@york.ac.uk

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**ABSTRACT:** Due to their particular geochemical properties and stability Rare Earth Elements (REE) can act as a 'fingerprint' for soils, and as a consequence have been employed in a variety of different archaeological scenarios in order to identify past human activities. In this study, for the first time, we apply REE signatures in different Spanish Neolithic settlements, all located in the Valle del Serpis region. More than 100 Neolithic settlements have been identified in this area, and most of these open sites are characterised by dark brown strata that are in contrast with the light brown soils of the valley. These dark brown deposits are usually covered by paleosols and have been interpreted as markers of anthropogenic activities. However, in order to demonstrate whether these strata are anthropogenic or natural features requires a better understanding of soil development processes. A total of fifty samples were taken across six different sites, and from each site the sampling was carried out at different depths through 3m deep sections. Four sites are clearly associated with archaeological findings (sites BF, LP, PB and AC); another one is from a natural section near the Neolithic site of Mas d'Is (MD) and has been radiocarbon dated to the beginning of the Holocene (7751-7611 cal BC); and the last corresponds to a place of uncertain attribution (BK). Major, minor and trace elements including REE were determined using XRF and ICP-MS, with Principal Components Analysis (PCA) used to statistically analyze these data. Results were then compared with the strata soil properties analysed by XRD and particle size analysis, and cross-referenced with archaeological data to aid interpretation. The results demonstrate that REE analyses provide significant details regarding anthropogenic activities and strata development history, and in this instance confirm and elaborate on the archaeological interpretation that these dark brown deposits are evidence of a region-wide agricultural system in the Neolithic Valle del Serpis.

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## MOLAB transnational access at the Estorick Collection: non invasive study of the Italian Futurist paintings.

Francesca Rosi<sup>\*A</sup>, Mattia Patti<sup>B</sup>, Ezio Buzzegoli<sup>C</sup>, Roberta Cremoncini<sup>D</sup>, Francesca Gabrieli<sup>A,#</sup>, Laura Cartechini<sup>A</sup>, Raffaella Fontana<sup>C</sup>, Diane Kunzelman<sup>G</sup>, Aldo Romani<sup>A,E</sup>, Chiara Anselmi<sup>E</sup>, David Buti<sup>A,§</sup>, Brunetto G. Brunetti<sup>A,E</sup>, Antonio Sgamellotti<sup>A,E,F</sup>, Costanza Miliani<sup>A</sup>

<sup>A</sup>CNR-ISTM, via Elce di Sotto, 8 Perugia, Italy; <sup>B</sup> Department of Civilisation and Forms of Knowledge, University of Pisa, via Pasquale Paoli 15, Pisa, Italy; <sup>C</sup>CNR-INO, Largo Enrico Fermi, 6 Firenze, Italy; <sup>D</sup>Estorick Collection of Modern Italian Art, 39A Canonbury Square, London, United Kingdom; <sup>E</sup>Centro SMAArt c/o Dipartimento di Chimica Biologia e Biotecnologie, Via Elce di Sotto 8, Perugia, Italy; <sup>F</sup>Accademia dei Lincei, Palazzo Corsini, Via della Lungara 10, 00165 Roma, Italy; <sup>G</sup>Opificio delle Pietre Dure (OPD), Via degli Alfani 78, Firenze, Italy.

# present affiliation National Gallery of Art, Washington DC

§ present affiliation CATS- SMK, Sølvgade 48-50, 1307 Copenhagen K, Denmark

\*francesca.rosi@cnr.it

**ABSTRACT:** A comprehensive campaign of non invasive spectroscopic analyses was carried out by the European facility MOLAB at the Estorick Collection in London. MOLAB is made of a unique array of non invasive portable equipment devoted to heritage science: since 2004 it offers transnational access to European researchers thanks to the support of EU projects: Eu-ARTECH, CHARISMA and currently IPERION CH ([www.iperion.eu](http://www.iperion.eu)). The study, motivated by the Italian Project FUTURAHMA (From Futurism to Classicism 1910-1922. Research Art History and Material Analysis), was focused on the collection of Futurist paintings which represents an exceptional example of the work produced by the artists affiliated with the F. T. Marinetti's movement during the first two years of their experimentation. In this study, imaging techniques, such as multispectral photography (VIS, IR, UV fluorescence, UV reflected) and multispectral infrared reflectography, provided for a comprehensive overview of the colour distribution and the execution technique of the Futurist paintings at the Estorick collection. Point-analysis techniques, namely X-ray fluorescence, medium and near FTIR, Raman and UV-vis reflection and emission spectroscopies, were employed for the chemical identification of the materials. The analytical approach was based on the use of the information from the point-analysis techniques, limited to a discrete number of points, as guideline for the interpretation of the Vis-NIR multispectral imaging results. A rich palette, including: blues (Thénard's, ultramarine, Prussian blue), purples (Mn and Co phosphates), yellows/oranges (lead chromate, Cd-based, ochre), greens (emerald green, Fe-based, viridian), whites (lead white, ZnO, TiO<sub>2</sub>), blacks (ivory black, Fe-based), and reds (vermillion, CdSSe, organic pigment), was identified. The combined study enabled to clearly point out how these identified pigments were used to produce the rich and variegated complex paints characteristic of these artworks. The integrated approach enabled to shed light on previously unknown features of the materials and techniques of the futurist painters solving historical questions on dating problems and revealing also the presence of a hidden painting under the Giacomo Balla's masterpiece "The hand of the violinist".

## Research of gesso and paint layers of the fresco painting of St. Christopher with a horse head from the Assumption Cathedral on the Sviyazhsk Island (Russia)

Rezida Khrumchenkova<sup>A,B</sup>, Polina Kaplan<sup>A,B</sup>, Airat Sitdikov<sup>A,B</sup>, Ilvina Biktagirova

<sup>A</sup> Restoration & Analytical Department, Institute of Archaeology, Tatarstan Academy of Sciences, Kazan, Russian Federation; <sup>B</sup> Centre of Excellence "Archaeometry", Kazan Federal University, Kazan, Russian Federation; <sup>C</sup> Center for collective use "Applied Nanotechnologies", Kazan National Research Technical University - KAI, Kazan, Russian Federation.

\* rkhrumch@gmail.com

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**ABSTRACT:** The work deals with one of the unique frescoes of the 16th century with a zoomorphic image of St. Christopher. Scanning electron microscopy was the main technology of presented scientific research. Features of the frescoes base and paint layers were determined as a result of investigations. One of a great number of saints revered by the Christians is martyr Christopher depicted on icons in a rather unusual manner. In Catholicism Saint Christopher (Christ-bearer) is portrayed as a giant carrying the blessing child across the river. In Orthodoxy there are three variations of Saint Christopher's icons. On certain images he is a fair young man with long hair and a four-point cross in his hand, and on others the Saint is portrayed in accordance with the Catholic canons. The most interesting and peculiar St. Christopher's icon is the one depicting him with a dog's or horse's head. In Russian icon painting, images of St. Christopher with a zoomorphic appearance are known since the second half of 16th and 17th centuries. These images include the fresco composition in the Cathedral of the Assumption of the Mother of God on the Island of Sviyazhsk (Russia). Its palette consists of seven colours. This signifies that the artwork was created in an early historical period, as starting from the 17th century fresco artists significantly increased the number of dye they used. The work includes a research of the gesso and paint layers of the fresco painting by means of optical and electron microscopy using Axio Observer Z1 and Axio Imager Z2m AURIGA CrossBeam with an Inca X-Max energy-dispersion spectrometer. Research samples were represented by fractures from variously coloured sections which contained both paint and the gesso base. The results of gesso research demonstrated that it was obtained using dolomite raw material. The research of paint layer fractures revealed numerous sections indicating that the wall painting has been subjected to restoration. The paints used by the ancient artists include samples of green and blue smalt. One of the dyes used for the purpose of refreshing the red stain was vermilion. The data obtained as a result of research using electron microscopy provided most valuable information for art experts, restorers and historians.

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## Screening of inorganic species using LA-ICP-MS imaging data and Raman spectroscopy for historic pigments identification.

Barbara Wagner<sup>\*A</sup>, Luiza Kępa<sup>A</sup>, Zofia Żukowska<sup>B</sup>, Anna Lewandowska<sup>C</sup>

<sup>A</sup>Faculty of Chemistry, University of Warsaw, Pasteura 2, 02-093 Warsaw, Poland; <sup>B</sup>Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664, Warsaw, Poland; <sup>C</sup>National Museum in Warsaw, Al. Jerozolimskie 3, 00-495 Warsaw, Poland

\*barbog@chem.uw.edu.pl

**ABSTRACT:** Detailed chemical information about favorite artistic materials and tools can be used for evaluation of works of art authenticity however it has to be connected with databases of reliable data about unquestionable original works of selected Authors. Systematic building of such database was started few years ago for the most famous Polish painters including Jacek Malczewski, Olga Boznańska and Jan Matejko. The historic and artistic value of their works remarkably limited possibilities for taking samples and only microscopic particles were taken. Depending on the structure and thickness of particular painting layers the amount and size of sampled particles varied from one object to the other. The decision about the way of sampling was made individually by the conservator. Micro-samples were taken from selected paintings representing a period of about 100 years at the turn of the XIX/XX centuries. This period of time is connected with intense changes in artistic materials production, and can be linked to the introduction of chrome pigments:  $\text{PbCrO}_4$  (1816);  $\text{BaCrO}_4/\text{SrCrO}_4$  (1830);  $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  (1838); cobalt pigments:  $\text{CoO} \cdot \text{ZnO}$  (1780);  $\text{K}_3[\text{Co}(\text{NO}_2)_6] \cdot \text{H}_2\text{O}$  (1852);  $\text{Co}_3(\text{AsO}_4)_2$  (1859);  $\text{CoO} \cdot \text{nSnO}_2$  (1860); cadmium pigments  $\text{CdS}$  (1907) or specific whites:  $\text{ZnO}$  (1834);  $\text{TiO}_2$  (1921). Pigments can be studied for various purposes, including dating or authentication of investigated objects, as well as for conservation diagnosis or getting knowledge about a particular artists palette. Many mineral pigments were synthesized during the 19<sup>th</sup> and at the beginning of 20<sup>th</sup> century. Between 1800 and 1950 many of new pigments were introduced to the market making this period of time particularly interesting. The aim of this work was to propose a flexible analytical approach for a quick screening of inorganic species in micro-samples of works of art for pigments identification.

Screening of inorganic species in micro-samples of pigments was based on visualization of the combined, chemical information obtained by means of Raman spectroscopy and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) imaging. Nicolet Almaga Raman spectrometer was used to collect spectra with laser excitation line  $\lambda=532$  nm. Laser ablation set up (LSX-213, CETAC) coupled to mass spectrometer (Nexion 300, Perkin Elmer) was used to register elemental imaging data. The combined molecular and elemental information was used to visualize the results. The proposed procedure was tested for 311 micro-samples of pigments. The evaluation of the analytical scenario allowing for getting the reliable results from the small amount of sampled materials was within the scope of this work. Mixtures reflecting variable artistic taste and individual susceptibility to artistic innovations was detected allowing for characterization of the personal favorite palette of the artists. The known dating of the object was expected to fit the history of the identified materials, otherwise the authenticity would be doubtful. Only one, out of all investigated paintings, was considered repainted or questionable and would not be included as the original in the database.

## Why does Geranium lake fade? Photochemical study of eosin-based pigments in oil paints

Annalisa Chieli<sup>\*A,B</sup>, Aldo Romani<sup>A,B</sup>, Brenda Doherty<sup>A,B</sup>, Chiara Anselmi<sup>A,B</sup>, Ilaria Degano<sup>C</sup>, Francesca Sabatini<sup>C</sup>, Costanza Miliani<sup>B</sup>

<sup>A</sup>Centro di EccellenzaSMAArt, Dipartimento di Chimica, Biologia e Biotecnologie, University of Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy, <sup>B</sup>Istituto CNR di Scienze e Tecnologie Molecolari (CNR-ISTM), Via Elce di Sotto 8, 06123, Perugia, Italy, <sup>C</sup>Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via Giuseppe Moruzzi 13, 56124, Italy

\*annipochi2@gmail.com

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**ABSTRACT:** This work is aimed at investigating the elusive nature of Geranium lake, the brilliant pink-scarlet hue eosin-based organic pigment widely employed by Vincent Van Gogh and his contemporaries. The rather impermanent nature of this lake in a large number of impressionist paintings is of current high concern for both curators and conservators scientists alike. Herein, the photochemistry of Geranium lake in an oil based medium has been investigated by means of UV-Vis reflectance/fluorescence and Raman spectroscopy integrated with HPLC-DAD-FD and LC-MS analyses. For this purpose, accelerated photo-ageing experiments irradiating with mono/polychromatic light have been carried out on oil paint models prepared with commercial eosin disodium salt and in-house aluminum and lead based eosin lakes alone and in admixture with different white pigments namely, zinc oxide and lead carbonate. Notably, the ageing experiment in the extended visible range confirmed not only the fugitive nature of Geranium lake but also evidenced that during a preliminary stage the bleaching process is partially reversible, suggesting the formation of an unstable leuco form of eosin. Targeted experiments using monochromatic light as well as a simplified eosin-oil system in solution, corroborated by the wide literature regarding the photophysics of xanthene dyes allowed us to hypothesize that the leuco form is created on photoreduction by exploiting the lipidic binder as the hydrogen donor. On the other hand, chromatographic analyses on bleached Geranium lake models using HPLC-DAD-FD and LC-MS revealed the formation of an uncolored brominated dihydroxybenzoyl-benzoic acid produced on fragmentation of the xanthene moiety. The results obtained in this study are of great importance in understanding the fading mechanism of Geranium lake and in highlighting the spectral/molecular markers for its detection in degraded paints.

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*Archeology & Cultural Heritage Session*  
***Arch&Heritage III***

(Mon. 12<sup>th</sup> of June, h. 14.45-16.00)

## Organic mass spectrometry to investigate molecular degradation phenomena of modern oil paintings.

Ilaria Bonaduce

Dipartimento di Chimica e Chimica Industriale, University of Pisa, via Moruzzi 13, Pisa

ilaria.bonaduce@unipi.it

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**ABSTRACT:** *The research performed until now in the framework of the JPI on Cultural Heritage project - Cleaning of Modern Oil Paintings (CMOP)- at the University of Pisa will be presented. The research is aimed at advancing our knowledge on the molecular causes and mechanisms behind modern oil paint vulnerability.*

*Until the 18<sup>th</sup> century, the paint production was at the basis of the activities in artists' ateliers: pure raw materials were purchased and then the paints were prepared according to traditional and sometimes secret recipes.*

*The Industrial Revolution brought rapid technological changes that profoundly affected art as well as any other sector. Although a large choice of new synthetic polymers became available as art materials, many 20<sup>th</sup> century artists continued to adopt drying oils as the binding medium for their artworks. With the development and diffusion of manufactured artists' materials, the 20<sup>th</sup> century has seen a significant evolution in artists' paint composition and technology. Oil-based paint media used by artists have expanded far beyond the traditional drying oils, including new drying and semi-drying oils. Metallic salts, metal soaps, and a wide variety of dispersion agents, plasticizers, fillers, surfactants, free fatty acids, waxes, proteins etc. were added to the paint formulations to produce different working proprieties such as viscosity, drying rate, and color.*

*Modern oil-based paintings, probably because of these innovations, are often proving to be unstable systems and present significant and often new problems: new reaction products are formed; colour changes are observed; migration and aggregation of selective chemical species occurs leading to the formation of vulnerable 'medium skins' on paint surfaces, as well as efflorescence, protrusions, and paint delamination. In addition, unpredictable water- and solvent-sensitivity occurs, as well as an alarming incidence of paint later liquidizing and beginning to drip across the surface of completed paintings.*

*The study is based on the use of mass spectrometric techniques for the analysis of the organic composition of modern oil paintings. To the aim, GC-MS and LC-MS based analytical procedures have been developed, to characterise of the molecular composition of paint samples, to evaluate the degree of hydrolysis, saponification and crosslinking of the oil media. These procedures have then been used to investigate the polymerisation, oxidation and crosslinking of oil binders on specifically prepared reference materials. Thermoanalytical techniques have also been used on simplified model systems to help the data interpretation.*

*The research here presented has been carried out at the Group of Analytical Chemistry for the Conservation of Cultural Heritage of the University of Pisa, in close collaboration with Judith Lee and Bronwyn Ormsby of Tate Britain, London, Klaas Jan van den Berg of Cultural Heritage Agency of the Netherlands, Amsterdam, and Donatella Banti and Aviva Burnstock, Courtauld Institute of Art, London.*

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## Atmospheric pressure MALDI for the non-invasive characterization of carbonaceous ink from Renaissance documents.

Giuseppe Grasso<sup>A</sup>, Marzia Calcagno<sup>A</sup>, Alessandro Rapisarda<sup>A</sup>, Roberta D'Agata<sup>B</sup>, Giuseppe Spoto<sup>\*A,B</sup>

<sup>A</sup>Department of Chemistry, University of Catania, V.le Andrea Doria 6, 95125, Catania, Italy; <sup>B</sup>Consorzio Interuniversitario I.N.B.B., c/o Department of Chemistry, University of Catania, Viale A. Doria 6, Catania, Italy.

\*gspoto@unict.it

*ABSTRACT: Spatially resolved analytical methods have significantly enhanced our capacity to study ancient works-of-art, since they cause minimal and, at times, no damage to the studied object [1-3]. Unfortunately, only a few analytical techniques operating within the requested spatial resolution are applicable for the investigation of organic components of artistic and archaeological objects. In recent years, possibilities offered by spatially resolved mass spectrometry (MS) techniques based on laser desorption ionization (LDI) has been highlighted [4]. However, direct LDI can be applied to study a limited range of different materials, while the use of matrices to assist laser induced ionization processes (matrix assisted LDI, MALDI) has expanded the applicability of the method also to the spatially resolved study of organic components of works-of-art [4].*

*The low-medium vacuum conditions required by MALDI-MS significantly limit its potential for in situ analysis of large objects. Atmospheric pressure MALDI-MS has been shown to overcome the above mentioned limitations and has been proposed as a new tool for the spatially resolved and minimally invasive analysis of organic components of artistic objects [5-7].*

*The present work demonstrates possibilities offered by in situ AP-MALDI-MS in identifying organic components of ancient carbonaceous inks. In particular, AP-MALDI-MS has been used for the first time to identify large polycyclic aromatic hydrocarbon (L-PAH) compounds from inks used in XVII century manuscripts. PAHs are formed as a consequence of an incomplete combustion of the organic matter. Therefore, their presence testifies that specific procedures were used in the past for the production of the carbonaceous material used as the pigment for inks.*

*We prove that it is possible to operate at AP, applying MALDI-MS as a suitable micro-destructive diagnostic tool for analyzing samples in air, simplifying the investigation of the organic components of artistic and archaeological objects.*

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## In situ characterization of the pictorial layers of an original 1771 Pascal Taskin harpsichord

Roxana Rădvan <sup>A</sup>, Ioana Maria Cortea\*<sup>A</sup>, Luminița Ghervase <sup>A</sup>, Lucian Ratoiu <sup>A</sup>, Monica Dinu <sup>A</sup>

<sup>A</sup>Department of Optoelectronic Methods and Techniques for Artwork Restoration and Conservation, National Institute for Research and Development in Optoelectronics, 409 Atomistilor St., Magurele, Romania.

\*ioana.cortea@inoe.ro

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**ABSTRACT:** The Peles National Museum in Sinaia, Romania, includes within its collection of musical instruments an original Taskin Pascal harpsichord dated 1771. The instrument is representative for the French harpsichords of the eighteenth century, having the keyboard in two registers, with floral paintings, gilded on the side, while the six panels of the wood case are painted in oil, with marine scenes, in the manner of Joseph Verne. With several degradations affecting both the paint layers and the wood case, a conservation strategy had to be developed. In this study we present a non-destructive, in situ characterization of the pictorial layers through various non-invasive diagnostic techniques: Multispectral Imaging, X-ray Fluorescence (XRF), Laser-Induced Breakdown Spectroscopy (LIBS) and Fourier Transform Infrared (FTIR) Spectroscopy. Analysis of the multispectral images acquired highlighted various past restoration interventions – fillings, consolidation and chromatic reintegration of the paint layer, as well as some interesting details related to the preparatory layer and on the artist's painting technique. On regard the materials used, preliminary results of the XRF and LIBS analysis suggests a rich colour palette: vermilion for the majority of the red areas, lead white, a copper based pigment for the blue and violet hues, various greens - iron oxide, chromium oxide and emerald green, along iron oxides for the red, yellow and ochre tones. FTIR analysis carried on particular areas of interest showed characteristic IR bands for proteinaceous binders, with egg yolk and possible traces of animal glue, while the varnish layer points towards a shellac resin. Results of the investigations offered valuable physico-chemical insights and conservation assessment, key information for the best restoration approach of this artifact with remarkable aesthetic and historic value.

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**ACKNOWLEDGMENT:** This work has been financed through The Sectoral Operational Programme “Increase of Economic Competitiveness” Priority Axis 2 – CDI: Operation 2.2.1. Project “Multisite Infrastructure for the Increase of Research and Development Capacity in the Field of Optoelectronics and Analytical Instrumentation – INOVA-OPTIMA” (Contract 658/07.08.2014 – SMIS 49164) and through the Core Programme, contract no. PN 16.40.01.01.



## Secondary mineral phases and ancient treatments on limestone from Monte de Prama nuragic statues (Sardinia, Italy)

S. Columbu<sup>A</sup>, S. Carboni<sup>A</sup>, S. Pagnotta<sup>B,C</sup>, M. Lezzerini<sup>B,C</sup>, S. Raneri<sup>C</sup>, S. Legnaioli<sup>B</sup>, V. Palleschi<sup>B</sup>

<sup>A</sup>Department of Chemical and Geological Sciences, University of Cagliari, Via Trentino, 51 – 09127 Cagliari, Italy

<sup>B</sup>Applied and Laser Spectroscopy Laboratory, Institute of Chemistry of Organometallic Compounds, Research Area of National Research Council, Via G. Moruzzi, 1 – 56124 Pisa, Italy

<sup>C</sup>Department of Earth Sciences, University of Pisa, Via Santa Maria, 53 – 56126 Pisa, Italy

columbus@unica.it

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**ABSTRACT:** The study intends to analyse with micro-destructive methods some original fragments of stone materials used in sculptures dated to Nuragic Age (XI-IX cent. BC) from Sinis area (Cabras, central-western Sardinia). The important nuragic sculptures, found in the archaeological site of Monte de Prama, consist of porous limestone surely locally quarried. Several historical, archaeological and geological studies have been already done on these sculptures, but up to date information and data on chemical and physical weathering processes occurring in the millennia, are missing.

The main purpose of this work is analysing by LIBS and SEM, well tested techniques in the Cultural Heritage field, the limestone finds from nuragic statues, first of all to know the degree of the chemical and physical alteration. Furthermore, the LIBS methodology, with the aid of XRD analysis of the particles adhering to the surface, allows us to analyse the composition of the films / coatings / incrustations present on the original surface of the statues (remained buried for centuries), and the definition of the secondary mineral phases not belonging to the limestone substrate. A careful compositional analysis of the surface also allows us to identify any original ancient treatments, aimed to colour the statues and / or conservation purposes to preserve and protect them from the weathering.

The chemical and physical alteration processes have been addressed through a comparative study of mineralogical, petrographic and physical characteristics among artifacts and geological samples from the Sinis area. Through PLT tests, He-pycnometry, Hg-porosimetry and BET analysis (by Brunauer-Emmet-Teller method) on field geological samples some physical and mechanical properties of the stone (density, porosity, specific surface area, resistance to compression, tensile, elastic modulus, etc.) were also determined to understand the resistance to tensional stresses in the original position of the sculptures. The analysis of the limestone alteration mechanisms also allows us to understand the ideal micro-environmental conditions in which to keep these important sculptures inside the museum spaces, to avoid further deterioration of the stone.

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# *Archeology & Cultural Heritage Session*

## ***Arch&Heritage IV***

*(Tue. 13<sup>th</sup> of June, h. 9.15-10.45)*

## X-ray fluorescence and Raman analytical techniques in written and artistic documents characterization

Marta Manso<sup>\*AB</sup>, Sofia Pessanha<sup>A</sup>, Mauro Guerra<sup>A</sup>, José Paulo dos Santos<sup>A</sup>, Maria Luísa Carvalho<sup>A</sup>

<sup>A</sup>LIBPhys-UNL, Laboratório de Instrumentação, Engenharia Biomédica e Física da Radiação, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516, Caparica, Portugal.

<sup>B</sup>Faculdade de Belas-Artes, Departamento de Ciências da Arte e do Património, Universidade de Lisboa, Largo da Academia Nacional de Belas-Artes, 1249-058 Lisboa, Portugal.

\*marta.sampaio@fct.unl.pt

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**ABSTRACT:** Paper and parchment have been for centuries the support of artistic and historic evidences. The analytical study of these supports and coloring materials gives historians and conservators the possibility of obtaining information on its material composition. This information not only helps in its safeguard but also in the comprehension of the artistic methodology of production, in the provenance and in the authentication issues and in the retrieval of hidden documents. X-ray fluorescence (XRF) and Raman spectroscopy are two complementary techniques suitable for the study of artistic and written documents due to its non-destructive character. XRF gives a quick highlight over the elements with a  $Z > 12$ , allowing the identification and the quantification of the existing elements in the supports and in the coloring materials. Raman spectroscopy enables detailed information about the organic and the inorganic composition of the pigments and the fillers. The research group has been developing XRF setups with different characteristics according to the needs of each heritage object type. Triaxial geometry equipments present a great advantage in the analysis of trace elements in low-Z matrix objects such as paper and parchment documents. This geometry significantly reduces the background of the measured spectra by eliminating the Bremsstrahlung produced in the X-ray tube through crossed polarization in the secondary target and in the sample. In this way, a better peak-to-background ratio is obtained, improving the detection limits and leading to higher sensitivity. Combined portable XRF and Raman setups are mostly required for in-situ analysis of historical and artistic documents that are not allowed to leave the museums or archives. In X-ray fluorescence spectrometry, the use of quantitative methods, independent of geometric and physical factors requires the use of standards of known composition, which should be as similar as possible to the unknown sample. The accuracy of this method depends on the number of standard samples used in the quantification and on the similarity of their composition with the unknown sample. A paper standards database consisting of well-known elemental composition paper samples is under construction enabling the elemental content determination of paper documents. In this talk, it will be presented the most relevant work developed by the research group concerning XRF setups development and quantitative methodologies applied to the study of written and artistic documents. It will cover 2D micro-XRF analysis of historical documents such as the 3<sup>rd</sup> Secret of Fátima, the coffee drawings by Lagoa Henriques and the hidden version of a book by Eça de Queirós. Quantitative results will be also presented for the supports and the inks characterization, and for helping in the comprehension of related degradation and authentication issues. Raman analytical applications to the study of coffee drawings and illuminated manuscripts will also be presented.

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## Time resolved photoluminescence spectroscopy for investigation of semiconductor modern pigments

Alessia Artesani\*<sup>A</sup>, Sara Mosca<sup>A</sup>, Austin Nevin<sup>B</sup>, Gianluca Valentini<sup>A</sup>, Daniela Comelli<sup>A</sup>

<sup>A</sup>Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardi da Vinci 32, 20133, Italy;

<sup>B</sup>INFN-CNR, Politecnico di Milano, Piazza Leonardi da Vinci 32, 20133, Italy.

[\\*alessia.artesani@polimi.it](mailto:*alessia.artesani@polimi.it)

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**ABSTRACT:** From the end of the eighteenth century, new artist pigments synthetically produced through industrial processes have been introduced. The conservator's interest in these modern pigments has been increased in the last decades especially because of their severe degradation following aging. The most significant issues are related to rapid deterioration and color-fading - like the famous example of Van Gogh 'Sunflower' series - that may occur especially if paints are conserved in poor conditions. A large number of scientists is nowadays working on the understanding and prevention of these degradation phenomena. The study of artist materials is however limited by their complexity. Pigments are not pure materials, they are generally mixed together and, more importantly, they are usually blended with binders. The interaction between metal ions and free fatty acid contained in organic binder lead to the formation of metal soaps, causing the alteration of painted layers, and thus degradation. A sub-group of modern pigments that show a particularly rapid degradation when mixed with oleic substances is those based on semiconductor material, as for example zinc white (based on ZnO). The physical characterization of these semiconductor pigments is made advantageous by their typical optical features. If properly light stimulated, they emit photoluminescence at different time regimes: the prompt emission (usually at nanosecond) is caused by direct band-to-band recombination, while the delayed emissions (at microsecond) instead are associated to the recombination from intra-band levels that act as trap states. In this scenario, time resolved photoluminescence (TRPL) spectroscopy is a great tool for the characterization of the photo-physical properties of semiconductor pigments. In recent years, our research group has focused its attention onto time-resolved characterization of this category of pigments as historical and laboratory-made samples. The time resolved technique has been developed for point-analysis to detect spectra and for imaging analysis for macro- and micro- investigation of heterogeneous surfaces. This work would be a report of the main achieved results. An illustrative example of TRPL micro-imaging will be provided through analysis of corpus of stratigraphic micro-samples from precious Russian modern paintings. In this case, time-gated spectral images of the PL emission has allowed the discrimination between different luminescent painted layers. Further, luminescence particles with a microsecond emission decay-kinetic were detected and ascribed to different crystal defects in painted layers. Apart from characterization of luminescent pigments, TRPL spectroscopy has proved to be an effective method for the detection of PL changes induced by material degradation. A remarkable example will be provided through the detection of changes occurring to trap state emissions in zinc white paints following carboxylates formation, which have been interpreted as due to novel crystal vacancies formation.

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## Protective effect of linseed oil varnish on archaeological wood treated with alum.

Jeannette J. Lucejko <sup>\*A</sup>, Jacopo La Nasa <sup>A</sup>, Caitlin M.A. McQueen <sup>B</sup>, Francesca Modugno <sup>A</sup>, Susan Braovac <sup>B</sup>, Maria Perla Colombini <sup>A</sup>

<sup>A</sup>Dipartimento di Chimica e Chimica Industriale, University of Pisa, via G. Moruzzi 13, Pisa, Italy; Department of Collection Management, Museum of Cultural History, University of Oslo, Oslo, Norway.

\* j.lucejko@dccci.unipi.it

**ABSTRACT:** The Viking Age wood artefacts recovered in the early 1900s from the Oseberg mound and treated with alum, are today highly degraded, a condition attributed to the effects of the alum-treatment and of the reactivity of alum and derived salts [1]. Some of the artefacts from Oseberg collection which were treated with alum, were also coated by linseed oil. Although the linseed oil did not fully penetrate the wood in many cases, these artefacts appear to be better preserved with respect to those not treated with linseed oil regarding their visual condition.

In order to assess the effect of the presence of linseed oil on wood preservation, alum treated woods coated with linseed oil were investigated. Fragments were sampled at different depths from the surface. Three analytical techniques, giving relevant information about the molecular composition and state of preservation of both archaeological wood and aged linseed oil, were adopted: gas chromatography coupled with mass spectrometry (GC-MS), pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and high-performance liquid chromatography coupled to electrospray ionisation and quadrupole time-of-flight mass spectrometry (HPLC-ESI-Q-ToF).

Specifically, Py(HMDS)-GC/MS was applied in order to assess the state of preservation of the main wood components in the presence of linseed oil and the alum treatment, while GC-MS and HPLC-ESI-Q-ToF were used to perform the lipid characterization and to investigate the lipid degradation and oxidation processes. Moreover characterisation of inorganic components of analysed material by XRD, FTIR and elemental analysis was performed.

The results showed that although the wood was highly depleted of carbohydrates [2], it was better preserved with respect to those artefacts not coated with linseed oil. Results from GC-MS and HPLC-ESI-Q-ToF together with those from Py-GC/MS suggested that the linseed oil played a mitigating role towards wood degradation. The behaviour of the lipid material, more oxidized on the wood surface respect to the depth section, suggested that the selective oxidation of the oil instead of the wood components in the aerobic environment led to a better preservation of the material. Furthermore, XRD, FTIR and elemental analysis gave information about the extent of alum impregnation and decomposition/transformation in the different regions of the fragments, providing further context for interpretation of the degree of wood degradation.

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## Total Reflection Near and Mid-Infrared Spectroscopic Studies on Outdoor and Archaeological Bronze Patinas.

Emilio Catelli<sup>\*A</sup>, Giorgia Sciutto<sup>§A</sup>, Jia Yiming<sup>#A</sup>, Silvia Prati<sup>%A</sup>, Rocco Mazzeo<sup>&A</sup>

<sup>A</sup>Department of Chemistry “G. Ciamician”, University of Bologna, via Selmi 2, Bologna, Italy;

\*emilio.catelli2@unibo.it

**ABSTRACT:** *The surface of a bronze artwork interacts with the surrounding environment and gradually develops brown and green patinas due to the formation of corrosion products. To protect the degraded external surface of bronzes, several organic materials (natural or synthetic) have been also applied. As a result, the composition of the external surface of either outdoor or archaeological bronzes results highly heterogeneous.*

*The characterization of surface compounds from the physico-chemical point of view is important in order to understand how the bronze has interacted with the environment as well as to determine the effectiveness of the treatments applied as protectives. It is also important in order to evaluate the correct maintenance of the artwork as well as to address, if necessary, the most suitable conservation approach.*

*So far, several spectroscopic techniques such as Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy (RS) have been used for the study of the superficial layers of bronzes. In particular, FTIR (4000-400 cm<sup>-1</sup>) has proved to be versatile for analyzing both organic and inorganic substances on bronzes and able to provide important information for the characterization of the different constituents.*

*In this research, we present the applicability of advanced methods in infrared spectroscopy based on the use of the near-infrared range for the study of outdoor and archaeological bronzes. In particular, total reflection FTIR in the extended range near and mid-infrared (6000-675 cm<sup>-1</sup>) and total reflection IR spectroscopy in the full near-infrared range (1000-2500 nm or 10000-4000 cm<sup>-1</sup>) have been applied as point analysis or imaging mode.*

*These advanced methods were tested on the outdoor bronze sculptures of the Neptune Fountain in Bologna (1566 A.D.) as well as on archaeological Chinese coins from the Northern Song Dynasty (960-1127 A.D.). The results show the possibility of using both total reflection near-infrared and near /mid-infrared range for the identification of the inorganic corrosion products and organic protective treatments on bronzes. In addition, characteristic marker bands in the near-infrared region can be used to recognize each different compound present in complex mixtures, when spectral features in the mid-infrared range are hidden due to the overlapping of diagnostic bands or to the distortion induced by total reflection acquisition mode.*



## micro-LIBS vs. XRF analysis of surface-enriched silver coins. Is a micro-destructive approach really unavoidable?

Vincenzo Palleschi<sup>A</sup>, Giuseppe Colucci<sup>B</sup>, Gioacchino Tempesta<sup>\*C</sup>

<sup>A</sup>Institute of Chemistry of Organometallic Compounds, CNR, Pisa, Italy; <sup>B</sup>Circolo Numismatico Pugliese. Sezione della Società di Storia patria per la Puglia Bari, Ateneo P.za Umbero I,1 Bari, Italy; <sup>C</sup>Dipartimento Department of Scienze della Terra e Geoambientali, University of Bari, Bari, Italy.

\*gioacchino.tempesta@uniba.it

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**ABSTRACT:** *We have performed a comparative study of micro-LIBS and X-Ray Fluorescence Spectroscopy (XRF) analysis for quantifying the silver contents in Swabian deniers minted during the Kingdom of Sicily (1194-1266). The combined use of the two techniques allowed us to validate the chemical composition of the coins and to valuate the altered surface and the surface-enrichment treatment eventually undergone. The use of LIBS coupled with microscope allowed to reduce the dimension of the laser-induced crater below 20µm so the visual aspect of the coin remains unchanged. The LIBS measures overcome the question of the surface alteration, but they do not represent the heterogeneity of the alloy because of the small sampling area. On the other hand, the XRF technique allows to analyze a larger surface, in a totally non destructive way; however, the sampling volume could be affected by alterations or excessive roughness. It has been verified that these two factors do not affect the reliability of the measures but could introduce an uncertainty in the quantity data. The LIBS quantitative data have been obtained using the One Point Calibration method (OPC) while the XRF quantitative data were obtained by means of the Fundamental Parameter method. A good agreement between the two results was found, demonstrating the effectiveness of both the micro-LIBS and XRF techniques, in spite of the above mentioned limitations. The comparative study has been conducted on a group of 50 deniers belonging to the reign of Henry VI and Frederick II; the results confirmed the knowledge about the devaluations of the coins within 50 years of the Swabian Kingdom. A classification method has been proposed to set historically the coins.*

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*Archeology & Cultural Heritage Session*  
***Arch&Heritage V***

*(Tue. 13<sup>th</sup> of June, h. 11.15-13.00)*

## X-ray micro beam: Cultural and archaeological heritage applications overview

M. L. Carvalho<sup>A\*</sup>, Marta Manso<sup>A</sup>, Sofia Pessanha<sup>A</sup>, A. Guilherme<sup>B</sup>, I Queralt<sup>C</sup>

<sup>A</sup>Laboratório de Instrumentação, Engenharia Biomédica e Física da Radiação (LIBPhys-UNL), Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, 2892-516 Caparica, Portugal; <sup>B</sup>BAM Federal Institute for Materials Research and Testing, 12200 Berlin, Germany; <sup>C</sup>Dept. of Geosciences, IDAEA-CSIC, Jordi Girona St., 18-26, 08034 Barcelona, Spain

\*luisa.carvalho@fct.unl.pt

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**ABSTRACT:** This work reviews the most used optical systems for X-ray microprobes and summarizes the experiences in research on Cultural Heritage with X-ray tube generators especially on polycapillary lens based systems.

The need for smaller beam spot sizes for various applications and the unique properties of X-rays have induced a remarkable and fast development in X-ray optical systems. These systems are divided into four main categories: reflective, absorbing, refractive and diffractive. Examples of the first two will be covered in this work, highlighting the properties that allow having spot sizes down to sub-micrometer regime.

An overview of the techniques that use such optical systems will be given, emphasizing their applicability on several case studies of Cultural and archaeological heritage.

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## Spectroscopic investigation of the interactions between commercial stains and protein matrices used in paintings

Sibilla Orsini<sup>\*A</sup>, Francesco Zinna<sup>A</sup>, Tarita Biver<sup>A</sup>, Lorenzo Di Bari<sup>A</sup>, Ilaria Bonaduce<sup>A</sup>,

Maria Perla Colombini<sup>A, B</sup>

<sup>A</sup>Department of Chemistry and Industrial Chemistry, University of Pisa, Via G.Moruzzi 13, Pisa

<sup>B</sup> Institute of Conservation and Promotion of Cultural Heritage of CNR, Via Madonna del Piano 10, Sesto Fiorentino

\*sibilla.orsini@gmail.com

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**ABSTRACT:** The aim of this study is to develop a detailed picture of the binding features of selected fluorescent tags towards proteins from artworks. Painters from all periods and across the globe have relied on a wide range of organic substances as painting materials, including proteinaceous materials, oils, saccharide gums and terpenoid resins. The development of specific methods for the stratigraphic localization and identification of proteins in paint cross sections is one of the most important steps to understand the painting technique of a work of art, to help understanding degradation phenomena, to identify the best conservation conditions. The stratigraphic localization of proteinaceous materials in art samples is still relatively arduous, due to the presence of inorganic materials (such as pigments), mixture with other organic materials and their degradation due to ageing (M.P.Colombini et al, Acc. Chem. Res. 2010, S.Dallongeville et al, Chem. Rev. 2016). Following a common technique, the sample is mounted on a cross-section, after embedding it in a synthetic resin, which is subsequently polished in order to expose the sample stratigraphy. Cross-sections can then be analyzed by imaging techniques based on magnetic resonance, mass spectrometry or optical spectroscopies (R.Clark, Chem. Soc. Rev.1995, S.Dallongeville et al, Chem.Rev. 2016). Fluorescence detection is by far the dominant detection method in the field of the microscopy imaging techniques due to a rapid signal acquisition and high detection sensitivity. Despite fluorescent tags are commonly used to reveal denatured proteins on gel electrophoresis, their use for the localisation of proteinaceous binders in paint cross sections still presents several drawbacks, as false negative and positive can occur (D.Magrini et al, Proc.Chem 2013, J.M.Messinger, JAIC 1992). In this work we present a spectroscopic investigation of the affinity of five commercial fluorescent tags with protein-based painting materials (egg white, casein from milk and animal glue), with the aim of better understanding the interactions taking place between commercial stains and protein matrices used in paintings, and thus of finding a reliable protocol for localising proteins in art samples. Beside fluorescence spectroscopy, we used for the first time circularly polarized luminescence (CPL) as a tool to reveal interactions in complex matrices relevant for the field of cultural heritage (S.Orsini et al, RSC Adv. 2016). We show that, in such cases, CPL provides unique information compared to more common techniques such as fluorescence and circular dichroism. These findings will contribute to provide a rational base to empirical observations in staining procedures.

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## Reducing Ablation and Improving Signal in Laser Induced Breakdown Spectroscopy by Using Spark Discharge in Sensitive and Valuable Samples

Mohammad Mahdi Hassanimatin\*, Seyed Hassan Tavassoli, Yaser Nosrati Qhods, Hadi Nozari

Institute of Laser and Plasma Research, University of shahid Beheshti, Evvin, Iran.

\*M\_Hasani Matin@sbu.ac.ir

*ABSTRACT: Laser induced breakdown spectroscopy (LIBS) is an analytical technique based on atomic emission spectroscopy of various samples. One way to reduce sample damage is reduction of laser energy. Reduction of laser energy reduce ablation along with signal intensity and reduction of laser energy less than a threshold leads to disappearing the spectrum. In this technique, sample damage is a disadvantage for analysis of some valuable and sensitive samples such as antiquities, bio and jewelry samples. In this paper, analytical performance of laser induced breakdown spectroscopy combined with spark discharge is studied for several samples. Because of the proximity to some antiquities samples, here, granite samples have been studied in air atmospheric pressure.*

*Signal intensity and signal to noise ratio in both LIBS and spark assisted LIBS (SA-LIBS) has been studied. In spark assisted laser induced breakdown spectroscopy (SA-LIBS) a laser pulse is used to ablate sample and form the plasma and simultaneously a spark discharge apply on the plasma. Spark discharge is used to reheat the laser plasma, to increase volume of laser plasma and to enhance the plasma emission.*

*In intensity of SA-LIBS spectral lines using low laser pulse energy is more intensive than LIBS ones with higher laser pulse energy. So in SA-LIBS technique, sample damage is much less than LIBS. In this method a considerable enhancement is observed in the intensity of spectral lines and the signal-to-background ratios with less ablation.*

*In order to investigate enhancement factors, plasma life-time, plasma temperature and electron density in two cases of LIBS and SA-LIBS have been calculated. Results show that applying electrical spark along with the LIBS leads to a significant increase in the signal intensity and signal to noise ratio. In LIBS and SA-LIBS, sample damage was investigated for the same energy of laser. As evidenced by the scanning electron microscope (SEM), size and amount of ablated material on the granite sample in the both cases is almost the same. As result during the electrical discharge in SA-LIBS hasn't ablation.*

## **The road map towards providing a robust Raman spectroscopy-based cancer diagnostic platform and integration into clinic.**

Riccardo Tagliapietra

Renishaw S.p.A., Pianezza (TO) – Italy

[www.renishaw.com](http://www.renishaw.com)

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*ABSTRACT: Over the last 15 years, Raman spectroscopy has been demonstrated to be able to distinguish healthy from cancerous tissues, and identify cancer stages and disease subtypes with high accuracy. These studies have been performed on a number of organs, such as the gastrointestinal (GI) tract, breast, brain, lymph nodes... The diagnostic accuracy surpasses our current gold standard. There is no doubt Raman spectroscopy can be a powerful cancer diagnostic tool. So the question we ask is: why isn't Raman spectroscopy adopted for routine cancer diagnostics yet?*

*The current gold standard of cancer tissue diagnostics remains to be haematoxylin and eosin (H&E) staining of suspect lesions. Since its introduction in 1837 by Wissowzky it remains to be the primary staining technique used today, despite being affected by subjectivity.*

*We propose for Raman imaging to be used as a cancer diagnostics tool, to identify cancer stages/subtypes through their spectral fingerprints, to extract chemical information and possibly lead to novel marker discovery. Imaging also provides spatial information, such as tumour margin analysis. Raman offers a means of removing the subjectivity of current diagnostics by providing an invariant and reproducible platform.*

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## **The first study of non-destructive technical to some manuscripts of Algerian heritage.**

Lynda Idjouadiene<sup>\*A</sup>, Toufik A. Mostefaoui<sup>A</sup>, Letizia Bonizzoni<sup>B</sup>, Marco Gargano<sup>B</sup>, Valeria Marzo<sup>B</sup>, Nicola Ludwig<sup>B</sup>

<sup>A</sup>Equipe LuMaNo, Laboratoire de Physico-Chimie des Matériaux et Catalyse, Université de Bejaia, 06000 Bejaia, Algerie; <sup>B</sup>Dipartimento di Fisica, Università degli Studi di Milan, via Celoria 16, 20133 Milano, Italia.

\*lynda.idjouadiene@univ-bejaia.dz

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*ABSTRACT: Knowledge of heritage objects is an important branch of art history. The analytical approach of these objects renews their study. Indeed, the identification of their constituent materials provides valuable and critical information in multiple related areas. The preservation of this wealth has to tackle inter alia the identification, localization, classification and restoration of these heritage objects. Historical pieces are unique and have often crossed centuries, or even millennia, making them extremely fragile. Handling them should be done with great skill. Any analysis should be non-destructive and ensure that no irreparable damage will be done for them. Thanks to scientific and technological advances this became possible, and a branch of physical chemistry has developed and has emerged: the Archeometry. The archeometry through these technical analyses can answer long unanswered questions. Unfortunately, our country (Algeria) is experiencing a marked delay in the introduction of these new techniques for the study and the preservation of our archaeological heritage. In this paper, we present a study of some manuscripts of Algerian heritage. We used XRF spectroscopy, FORS and ATR to characterize these manuscripts to study and discuss the materials (inks and pigments) that were used. The combined analytical approach has shown that the pigments identified include vermilion, Prussian blue, iron gall ink and a mixture of yellow Indian with ocher.*

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## **A unique 10th century silver coin of the Banijurid dynasty (Bolgar settlement, Russia)**

Eugenia Shaykhutdinova<sup>\*A-C</sup>, Rezida Khamchenkova<sup>A,B</sup>, Rinat Khasanov<sup>B</sup>, Airat Sitdikov<sup>A,B</sup>,

<sup>A</sup> Restoration & Analytical Department, Institute of Archaeology, Tatarstan Academy of Sciences, Kazan, Russian Federation; <sup>B</sup> Kazan Federal University, Kazan, Russian Federation; <sup>C</sup> Department of Technology of Machinery Production, Kazan National Research Technical University named after A.N.Tupolev - KAI, Kazan, Russian Federation.

\*eugen.shaykhutdinova@gmail.com

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### **ABSTRACT:**

*For several centuries Bolgar was a trade and economic centre of the Volga region, which is indicated by numerous archaeological findings. A large portion of the discovered Kufic coins were minted by rulers of the Samanid dynasty. A study of silver-containing coins minted by this dynasty using scanning electron microscopy and emission spectral analysis allowed to discover a unique 10th century silver and bismuth dirham minted by a Samanid vassal from the Banijurid dynasty.*

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# *Environment Session*

## ***Envir I***

*(Mon. 12<sup>th</sup> of June, h. 9.45-10.45)*

## Oxygenated and nitrated PAHs in the atmosphere of Buenos Aires. Determination by UHPLC(+)-APCI-MS/MS

Fabián Fujiwara<sup>A</sup>, María Evangelina Guíñez<sup>A,B</sup>, Soledad Cerutti<sup>\*A,B</sup>,  
Darío Gómez<sup>C</sup> and Patricia Smichowski<sup>\*A,C</sup>

<sup>A</sup>Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Godoy Cruz 2290, C145FBA, Buenos Aires, Argentina, <sup>A,B</sup>Instituto de Química de San Luis (CCT-San Luis), Laboratorio de Espectrometría de masas, Ejército de los Andes 950, CP5700, San Luis, Argentina, <sup>C</sup>Comisión Nacional de Energía Atómica, Gerencia Química, Av. Gral Paz 1499, B1650KNA, Pcia. Buenos Aires, Argentina.

\*smichows@cnea.gov.ar

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**ABSTRACT:** Oxygenated and nitrated polycyclic aromatic hydrocarbons (OPAHs and NPAHs) were determined in PM<sub>2.5</sub>, PM<sub>10</sub>, and tree barks samples collected in Buenos Aires, Argentina. Different strategies were followed for the collection of fine and coarse fractions including type of filters and samplers. Samples of PM<sub>2.5</sub> were collected on glass fiber filters with a medium volume sampler while for PM<sub>10</sub> glass and quartz fiber filters high volume sampler were used. For PAHs derivatives quantification ultra high performance liquid chromatography-atmospheric pressure chemical ionization tandem mass spectrometry (UHPLC-APCI-MS/MS) was used. Data acquisition under MS/MS was achieved by applying multiple reaction monitoring to provide a high degree of sensitivity and specificity. The chromatographic separation was carried out on a reverse phase rapid resolution column using a gradient mode. In APM, four PAHs derivatives were detected at concentrations ranging from 0.01 to 240.62 ng m<sup>-3</sup>.

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## Thallium speciation in acid mine drainages: method development, influence of environmental parameters and application.

Beatrice Campanella<sup>\*A</sup>, Lorenzo Biancalana<sup>B</sup>, Corinne Casiot<sup>C</sup>, Massimo Onor<sup>A</sup>, Martina Perotti<sup>D</sup>,  
Riccardo Petrini<sup>D</sup>, Emilia Bramanti<sup>A</sup>

<sup>A</sup>Istituto di Chimica dei Composti Organometallici, Consiglio Nazionale delle Ricerche, via Moruzzi 1, Pisa, Italy; <sup>B</sup>Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Moruzzi 13, Pisa, Italy; <sup>C</sup>Hydro-Sciences Montpellier, UMR 5569 CNRS-IRD-UM, CC57, 163, rue Auguste Broussonnet, Montpellier, France; <sup>D</sup>Dipartimento di Scienze della Terra, Università di Pisa, via S. Maria 53, Pisa, Italy

\*beatrice.campanella@pi.iccom.cnr.it

**ABSTRACT:** The increasing presence of thallium in the environment is attracting some attention because of its growing demand by modern high-technology industries. Thallium is more toxic than mercury, cadmium, copper, lead, and zinc, and its aquatic toxicity is apparently not affected by water hardness or humic acid concentration.

Tuscany (Italy) was one of the Italian regions that experienced a significant mining activity, which left a legacy of environmental problems related to acid mine drainages. The finding in 2014 of high Tl concentrations in drainages from abandoned mining districts located in the northwest of Tuscany posed some concern related to the potential dispersion of this element in the environment. The study of thallium redox speciation appears a way to understand its environmental behavior, since the valence state of thallium determines its toxicity, distribution and mobility.

In this work, the speciation of thallium in acid mine drainages, surface waters and springs in the mining catchment of Valdicastello Carducci (Tuscany, Italy) was first determined after separation with ion chromatography and online detection with ICP-MS. Successively, adopting a natural water sample collected from a mine drainage rich in thallium and iron as model, the distribution of aqueous Tl(I)/Tl(III) as a function of light exposure and solution properties was studied.

None oxidation of Tl(I)(aq) took place when natural water sample was exposed to sunlight. In the system with an excess of Mn(IV) oxide a quantitative oxidation of Tl(I)(aq) was observed, notably at pH 3.3 (original pH of sample 2.1), both for the sample kept in the dark and the sample exposed to solar light. The process is not reversible, as indicated by results for samples kept in the dark for one week. Direct irradiation with a low-pressure mercury lamp or with a visible light-emitting diode (LED) also lead to oxidation of Tl(I)(aq), but not quantitatively. In these cases, the process is partially reversible by keeping the sample in the dark. It is suggested that adsorption of thallium to the Fe/Mn oxyhydroxides determines the rate of oxidation.

The study can provide an important scientific groundwork for the handling of thallium pollution.

## Customized reference compounds for the determination of pollutants, metabolites and residues of chemical manufacturing

Matteo Gentili<sup>\*A</sup>, Alessandro Bonari<sup>B</sup>, Ilenia Pompilio<sup>B</sup>, Stefano Dugheri<sup>C</sup>

<sup>A</sup>Giotto Biotech S.r.l., via Madonna del Piano 6, 50019 Sesto F.no, Italy; <sup>B</sup>Dipartimento di Medicina Sperimentale e Clinica, University of Florence, Largo G.A. Brambilla 3, 50139 Firenze, Italy; <sup>C</sup>Laboratorio di Igiene e Tossicologia Industriale, Azienda Ospedaliero-Universitaria Careggi, Largo P. Palagi 1, 50100 Firenze, Italy.

\*info@giottobiotech.com

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*ABSTRACT: Over the last decades, much effort has been dedicated to the implementation of new analytical techniques and methods for the reliable identification and quantification of substances in the most different matrices.*

*At the same time, the discovery and put-in-practice on a routinely basis of these sensitive and easy to use methods have uncovered a variety of new analytes, whose concentration needs to be kept under control in order to guarantee an adequate safety level, especially in the workplace. New harmful compounds, metabolites, food contaminants and pollutants are discovered every day and need to be fully characterized; furthermore, new methods must be developed for their precise quantification.*

*In this context, Giotto Biotech aims at meeting the need for new and unavailable molecules to be used as reference compounds, by offering a dedicated service of custom organic synthesis of natural and isotopically enriched compounds (D, <sup>13</sup>C, <sup>15</sup>N).*

*In this contribution we wish to present some examples of custom made molecules which have been synthesized by Giotto Biotech on customer's request, and have been successfully employed as standards for the determination of analytes in different scenarios.*

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# *Environment Session*

## ***Envir II***

*(Mon. 12<sup>th</sup> of June, h. 11.15-13.00)*

## Compound Methodology for the Characterization of Lead Contamination in Soil: The Case of a Former Battery Factory in Monterrey, Mexico

Ricardo Urrutia-Goyes<sup>\*A</sup>, Ariadne Argyraki<sup>B</sup>, Nancy Ornelas-Soto<sup>C</sup>

<sup>A</sup>Universidad de las Fuerzas Armadas ESPE, Sangolqui, Ecuador; <sup>B</sup>Faculty of Geology and Geoenvironment, National and Kapodistrian University of Athens, Athens, Greece; <sup>C</sup>Laboratorio de Nanotecnología Ambiental, Tecnológico de Monterrey, Monterrey, México.

\*erurrutia@espe.edu.ec

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*ABSTRACT: Former battery factories have created environmental and health problems for years and the exposure to lead in surface soils has been underestimated. The identification of lead contamination and distribution at existing sites is crucial. Characterization processes are generally performed using inductively coupled plasma mass spectrometry (ICP-MS) to measure the concentration of metals in soil samples. However, alternative techniques such as x-ray fluorescence (XRF) have been used lately in environmental studies as it allows to take readings in the field in a prompt manner, despite its lower accuracy and higher detection limits regarding the former. In this study, a former battery factory site in Monterrey, Mexico has been analyzed in order to detect lead pollution. Contaminated soils were characterized by using a novel hybrid methodology composed of both aforementioned techniques. Samples were taken in 205 locations and analyzed using a portable XRF device after a simple homogenization process, whereas 24 of these samples were analyzed using ICP-MS according to international sampling guidelines. The two techniques were compared and contrasted in order to define a compound methodology, which encompasses their respective advantages. Finally, a hybrid map of the contamination distribution was devised and areas of concern were calculated.*

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## Detection of Volatile Organic Compounds in direct current pulse glow discharge plasma by Soft Plasma Ionization Mass Spectrometry

Yoko Nunome<sup>\*A</sup>, Kenji Kodama<sup>B</sup>, Yasuaki Ueki<sup>C</sup>, Ryo Yoshiie<sup>D</sup>, Ichiro Naruse<sup>C</sup>, Kazuaki Wagatsuma<sup>E</sup>

<sup>A</sup>Graduate school of Integrated Arts and Sciences, Hiroshima University, 739-8521, Japan; <sup>B</sup>X-ray Instrument Division, Rigaku Corporation, 569-1146, Japan; <sup>C</sup>Institute of Materials and Systems for Sustainability, Nagoya University, 464-8603, Japan; <sup>D</sup>Graduate School of Engineering, Nagoya University, 464-8603, Japan; <sup>E</sup>Institute for Materials Research, Tohoku University, 980-8577, Japan.

\*nunome@hiroshima-u.ac.jp

**ABSTRACT:** This study describes a measuring system for mass spectrometry, consisting of a glow discharge ionization source driven by pulsed dc voltage for soft plasma ionization and a mass spectrometer, to detect volatile organic compounds rapidly and easily. To suppress fragmentation of the organic compounds, several discharge parameters (discharge current, discharge pressure, pulse frequency and duty ratio) were varied to determine the optimal conditions for softer ionization. Gaseous organic components, known as toxic volatile organic compounds (VOCs), are oxidized by photochemical reaction in air, leading to produce carboxylic acids and their derivatives. These oxidized products may form atmospheric organic aerosols (secondary organic aerosols; SOA) by gases condensations in the atmosphere. Organic aerosols have serious implications for the environment and human health. In the previous study, we directly detected organic components in smoke by soft plasma ionization (SPI) –mass spectrometry (MS) with a glow discharge ionization source [1]. The main ionization mechanism in the SPI–MS system was considered, in which organic molecules could be readily ionized by Penning ionization with  $N_2^+$  species. However, organic components in smoke were fragmented in the air plasma. Fragmentation problems hindered organic components of higher molecular weight to be distinguished easily. In this study, the glow discharge was driven by a pulsed direct-current voltage to suppress fragmentation of high-molecular-mass compounds. Vapor from an organic solvent was measured for sampling of VOCs to evaluate the basic characteristics of the pulsed dc SPI source. The detectable signals for VOCs vapor were examined when varying important discharge parameters such as discharge current, discharge pressure, pulse frequency and duty ratio of the SPI discharge. The mass spectra obtained from the organic solvents exhibited their molecular ion peaks  $[M^+]$  as the major peak with little or no fragmentation under the optimal conditions. The spectral intensity tended to increase with increasing the discharge pressure at a constant discharge current. Chemical species in the SPI source will be analyzed by using emission spectroscopy to consider the ionization mechanisms

### Reference

[1] Y. Nunome, K. Kodama, H. Park, K. Matsumo, S.C. Lee, K. Kitagawa, *Microchem. J.*, 99, (2011), 470–477.

## Determination of selected trace elements in the open ocean.

Emilia Vassileva <sup>A\*</sup>, Irena Wysocka <sup>A,B</sup>

<sup>A</sup>International Atomic Energy Agency, Environmental Laboratories, 4 Quai Antoine 1<sup>er</sup>,  
98000 Monaco

<sup>B</sup>Polish Geological Institute National Research Institute, Rakowiecka 4, 00-975 Warsaw, Poland

\* e.vassileva-veleva@iaea.org

**ABSTRACT:** The importance of trace elements and their role in biological cycling has become evident in recent years. Particular attention has been focused on iron as it has been well established that the supply of Fe limits the total productivity in high nutrient low chlorophyll regions of the surface ocean. Zn, Ni, Cu, Co and Cd display similar behavior to the macronutrients, nitrate, phosphate and silicate, indicating their involvement in biological cycles. In addition, Mn and Pb are important tracers of possible natural or anthropogenic inputs through aerosol deposition and/or lateral transport from continental margins. Despite the significance of these trace metals, an understanding of the biogeochemical cycles or even the global distribution of these trace metals is still limited. A more comprehensive understanding of trace metal biogeochemical cycles is therefore critically needed. Accurate and precise quantification of trace elements in the open ocean and seawater samples remains a difficult task, due to low analytes concentrations (typically below  $1\mu\text{g L}^{-1}$ ), very complex matrix ( $\sim 3.5\%$  TDS), potential spectral interferences, and possibility of contamination during sampling or sample preparation step. The direct analysis of seawater by ICP-MS is usually hampered by the complex matrix that may cause significant non-spectral interferences in the plasma resulting in signal suppression. Pre-concentration and or/separation procedures have been proposed as efficient solutions to overcome this problem. A method based on the application of Isotope Dilution Inductively Coupled Plasma Mass Spectrometry (ID ICP-MS), applied as a primary method of measurements was developed and applied for the determination of Fe, Ni, Cu, Zn, Cd, and Pb in the open ocean samples. For the monoisotopic elements Mn, Co method based on preliminary matrix separation, external calibration approach combined with internal standard was used. An automated off-line seaFAST pre-concentration system with integrated column containing chelating resin was applied in the sample pre-treatment step. Selected trace elements were simultaneously and quantitatively pre-concentrated from 10 mL of seawater sample spiked with enriched isotopes, eluted with 200  $\mu\text{L}$  of 1.8 M  $\text{HNO}_3$ , and determined by Sector Field ICP-MS. The single-step pre-concentration removed more than 99.9% of Na, K, Mg and Ca from seawater. ISO-17025 and Eurachem guidelines were followed to perform the validation of the proposed methodology. The estimation of the total uncertainty associated to each measurement result was fundamental tool for sorting the main sources of measurement biases. Preliminary forecast of the uncertainty budgets was used as a strategy to ensure that determination of trace elements in seawater could be achieved with demonstrated traceability to a stated system of reference within less than 10 % expanded uncertainty ( $k=2$ ) respectively. The method was validated through the analysis of certified reference material NASS-6, CAAS-5 and SLEW-3 from the NRC Canada. Additional validation of the developed analytical procedure was effectuated by comparison with the values reported in the frame of EC JRC IRMM IMEP-40 exercise on the determination of trace elements in seawater.

## **Ion Chromatography Coupled Multicollector/ICP MS in the Determination of Inorganic Cations**

Agnieszka Anna Krata<sup>A\*</sup>, Jakub Karasinski<sup>A</sup>, Ewa Bulska<sup>A</sup>, Marcin Wojciechowski<sup>A</sup>, Ludwik Halicz<sup>A,B</sup>

<sup>A</sup>Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, Zwirki i Wigury 101, Warsaw, 02-089, Poland; <sup>B</sup>Geological Survey of Israel, 30 Malkhei Israel st., Jerusalem 95501, Israel

\*kratka@chem.uw.edu.pl

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*In this work the applicability of Ion Chromatography (IC) coupled to Multicollector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS) for on-line isotope ratio analysis of various elements like: Sr, Mg and Ca was explored. The effective separation of Sr from matrix by IC enables on-line isotopic analysis of  $^{87}\text{Sr}/^{86}\text{Sr}$  by MC-ICPMS, without the need in a laborious off-line, time consuming sample preparation and clean room facilities. Mass discrimination and instrument drift were corrected by the use of the natural constant  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio as an internal standard. The precision ( $2\sigma$ ) of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.003% was achieved in natural samples. Various instrumental setups were employed to enable continuous Mg or Ca separation from the sample matrix by IC followed by MC-ICPMS. The performance of two separation columns IonPac CS16 (ID 5 mm or ID 3 mm) connected with appropriate CERS 500 suppressors (4 mm or 2 mm) using dry and wet plasma conditions was compared. With the use of ID 3 mm column and 2 mm suppressor it was possible to apply dry plasma mode with Aridus II desolvation system. Mass discrimination and instrument drift were corrected by sample-standard bracketing method using the  $^{26}\text{Mg}/^{24}\text{Mg}$  isotope ratio of DSM-3 as standard. Good accuracy and high precision of the magnesium isotope ratio (generally 0.15 ‰ (2SD)) were achieved for wet and dry plasma modes; both were comparable to off-line Mg separation and continuous measurement. In case of calcium mass discrimination and instrument drift were corrected by sample-standard bracketing method using the  $^{44}\text{Ca}/^{42}\text{Ca}$  isotope ratio of NIST-915a as standard. Robustness and applicability of the method was demonstrated for matrix-rich natural water and rock samples isotope analysis, respectively.*

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*Acknowledgements: Financial support from National Centre of Science (NCN, Poland), project UMO-2014/13/B/ST4/04503, in the years 2015 - 2018, is gratefully acknowledged. The study was carried out at the Biological and Chemical Research Centre, University of Warsaw, established within the project co-financed by European Union from the European Regional Development Fund under the Operational Programme Innovative Economy, 2007 - 2013.*

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## Impact of soil and root type on the behavior of ZnO and Al<sub>2</sub>O<sub>3</sub> by microbial and antioxidant activity.

Asli Baysal<sup>\*A</sup>, Hasan Saygın<sup>B</sup>, Gul Sirin Ustabasi<sup>A</sup>

<sup>A</sup>Medical Laboratory Technics, Health Services Vocational School of Higher Education, T.C. Istanbul Aydin University, Sefakoy Kucukcekmece, 34295 Istanbul, Turkey <sup>B</sup>Application and Research Center for Advanced Studies, T.C. Istanbul Aydin University, Sefakoy Kucukcekmece, 34295 Istanbul, Turkey

\*aslibaysal@aydin.edu.tr

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**ABSTRACT:** Various applications of metal oxide nanoparticles could result in their accumulation in soil, air and water threatening terrestrial ecosystem. Several reports have shown the effects of metal oxide nanoparticles on soils and plants. The environmental impacts of nanoparticles are still not well understood. In this study, we investigate the microbial (number of bacteria, bacteria type and spore formation) and antioxidant responses of different soil and different root type of plants by exposure of zinc oxide and aluminum oxide nanoparticles. For this purpose, different plants which belongs various root (tap-roots, tubers, bulb) were cultivated in two agricultural soil irrigated with and without zinc oxide and aluminum oxide nanoparticles at 0, 1, 20 mg/L during 4 weeks. Nanoparticles were applied every week at various doses in soil starting with cultivation until harvesting. The behavior of nanoparticles in different agricultural soil and their effect on different root plants were investigated by microbial and antioxidant activity. Nanoparticles increased the microbial and antioxidant activity. The soil type affected the intensity and capacity of nanoparticle. The bacteria activity was correlated spore formation in soil by exposure of nanoparticles. Spore formation improved the immunity of organism and obtained survival unfavorable conditions, on the other hand spore formation provided the medium for bacterial infectious disease. To our knowledge, this is the first study comparing effects of nanoparticles on different root plants and soils by microbial and antioxidant activity.

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## Chemical compositional bulk analysis of size-segregated aerosol particles using ATR-FTIR

Li Wu<sup>\*A</sup>, Hee-seung Chae<sup>A</sup>, Abdul Malek<sup>A</sup>, Hyeonsu Kim<sup>A</sup>, Chul-un Ro<sup>A</sup>

<sup>A</sup>Department of Chemistry, Inha University, Incheon, South Korea;

\*ws19910130@yahoo.com

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**ABSTRACT:** The bulk chemical composition of size-segregated aerosol particles can provide valuable insights into their reactivity, sources, and fate in the troposphere. In this work, aerosol samples were collected at the roof of a building in KRISS (Korea Research Institute of Standards and Science; 36.39°N, 127.37°E) located at Daejeon city, Korea, where industrial and anthropogenic activities are expected to mainly influence the chemical compositions of aerosol particles. Size-segregated aerosol particles were collected on Ag foil using a seven-stage May cascade impactor with aerodynamic cut-off diameters of 16, 8, 4, 2, 1, 0.5, and 0.25  $\mu\text{m}$  for stages 1-7, respectively. The sampling duration for each stage was set differently to collect enough particles for bulk analysis using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) technique. A Universal ATR single reflection accessory, comprising a diamond/KRS-5 internal reflection element (IRE) crystal with a diameter of 1.8 mm, installed in Perkin Elmer Spectrum 100 FTIR spectrometer, was used for the bulk analysis. A home-made curve-fitting program was utilized for deconvolution of asymmetric ATR-FTIR peaks in order to obtain areas of the characteristic IR peaks for relative quantitative analysis. Quantitative low-Z particle EPMA (energy dispersive electron probe X-ray microanalysis) provides complementary information on elemental concentrations, including IR inactive species such as NaCl. For supermicron particles (stages 1-4), major chemical species are aluminosilicates, carbonates, and organics, while submicron particles (stages 5-7) are abundant with  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ , and organics. The mixing ratios of chemicals varies with particle size and time. For example, for the submicron fraction, nitrate peak relative intensity increases during peak office hours, due to increased traffic emissions compared to other time in the day or night. Further analyses involving variation of chemical composition and mixing ratio and state with time and size fraction are under progress, aiming to give more detailed understanding about the aerosol characteristics.

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## Real-Time Investigation of Chemical Compositions and Hygroscopic Properties of Aerosols Generated from NaCl and Oxalic Acid Mixture Solutions Using in Situ Raman Microspectrometry.

Xue Li<sup>A</sup>, Jisu Lee<sup>A</sup>, Hyo-Jin Eom<sup>A</sup>, Han-Jin Yoo<sup>A</sup>, and Chul-Un Ro<sup>A\*</sup>

<sup>A</sup>Department of Chemistry, Inha University, Incheon, Korea

\*curo@inha.ac.kr

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**ABSTRACT:** Recently, ambient sea spray aerosols (SSAs) were reported to undergo reactions with dicarboxylic acids (DCAs). The hygroscopic properties of SSAs could be altered when the chemical compositions of SSAs are modified, which in turn alters their optical properties and cloud-droplet nucleation efficiency. Among water-soluble DCAs, oxalic acid (OA) is most abundant, in atmospheric aerosols followed by succinic acid and malonic acid. In this work, the hygroscopic behavior and chemical reactivity of aerosols generated from NaCl-OA mixture solutions were studied using in situ Raman microspectrometry (RMS). The change in size, chemical composition, and phase as a function of the relative humidity (RH) for individual aerosols were simultaneously monitored. The hygroscopic measurement was performed first through a dehydration process, followed by a humidification process. Raman spectra showed that monosodium oxalate (MSO) was formed due to the chemical reaction between NaCl and OA from solutions of NaCl:OA = 3:1 and 2:1 after particles were generated. As RH decreased, disodium oxalate (DSO) was produced during the dehydration process. The aerosols generated from the solution of NaCl:OA = 3:1 and 2:1 showed single efflorescence, where MSO and DSO were in crystalline forms. Deliquescence transition of unreacted NaCl moiety was around 76% and complete dissolution of MSO and DSO was not observed even at RH > 98%. For the aerosols from NaCl:OA = 1:1 and 1:2 solutions, MSO was formed after generation. No deliquescence transition was observed for the aerosols from NaCl:OA = 1:1 and 1:2 solutions and water absorption started at RH > 95%. The observed different hygroscopic behavior was due to the different contents of NaCl, OA, MSO and DSO in the aerosols. Real-time investigation of chemical compositions of aerosols from NaCl-OA mixture solutions was investigated for first time by in situ RMS and quantitative analysis of chemical compositions during hygroscopic measurement are under investigation.

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# *Environment Session*

## ***Envir III***

*(Thu. 15<sup>th</sup> of June, h. 9.15-10.45)*

## Arsenic speciation in certified reference materials

Zoltan Mester<sup>A\*</sup>, Phuong-Mai Le<sup>A</sup>, Jianfu Ding<sup>A</sup>, Donald M. Leek<sup>A</sup>, Juris Meija<sup>A</sup>, Gilles Robertson<sup>A</sup>,  
Anthony Windust<sup>A</sup>, Tomas Matousek<sup>B</sup>

<sup>A</sup>National Research Council Canada, 1200 Montreal Rd. Ottawa, Canada; <sup>B</sup>Institute of Analytical Chemistry, The Czech Academy of Sciences, Brno, Czech Republic

\*Zoltan.mester@nrc.ca

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*ABSTRACT: Development of certified reference materials for arsenic speciation has been in the focus research at NRC Canada for over thirty years. In the presentation an overview will be given on historic developments on arsenic speciation in marine organism and the latest results on novel reference materials for arsenic speciation will be discussed. Speciation arsenic in water and sea water reference materials certified to contain low / sub ppb total As was performed. Methylated As species at the low ppt were observed using a HG-CT-ICP-MS system. The analytical process and the figures of merits will be presented and discussed. Results will also be presented on the characterization of suit of three arsenobetaine-certified reference materials by quantitative NMR. We have synthesized an arsenobetaine bromide high-purity standard of natural isotopic composition and two carbon-13-labeled isotopic standards. Assignments of the chemical purity and isotopic composition are not trivial in the case of arsenobetaine, and in this study we utilized quantitative <sup>1</sup>H-NMR techniques for the determination of the mass fractions (chemical purity). The isotopic purity of all three standards was also assessed by NMR from the carbon-13 satellite signals. The standards are non-hygroscopic, high purity (ca. 0.99 g/g), and the carbon-13 enrichment for both isotopic standards is  $x(^{13}\text{C}) \approx 0.99$ . These standards are designed for use as primary calibrators for mass spectrometric determination of arsenobetaine in environmental samples.*

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## Novel Methods for Speciation Analysis of Chromium in Environmental Samples Based on Solid Phase Extraction and Ion-exchange Chromatography Coupled to Atomic Spectrometry

Barbara Leśniewska\*, Beata Godlewska-Żyłkiewicz, Laura Trzonkowska

\*Institute of Chemistry, University of Białystok, 15-245 Białystok, Ciołkowskiego 1K, Poland

\*blesniew@uwb.edu.pl

*The speciation analysis of chromium in environmental samples is of great importance due to different biological activity of Cr(III) and Cr(VI) species, their chemical behavior and toxic effects on humans and other living organisms as it is well known that Cr(VI) possess carcinogenic and mutagenic properties. However the chromium speciation analysis, even in surface and waste waters, is still a difficult analytical task. Main problems are associated with the low concentration of analytes, their transformation and strong influences of a complex sample matrix on analytical signal of chromium. Therefore, in order to obtain accurate and reliable results of speciation study, the analytical methods should combine the selective and efficient isolation/separation procedures of chromium species with their sensitive determination.*

*In this work new methods for speciation analysis of chromium in environmental samples based on separation of chromium species by solid phase extraction and their determination by atomic absorption spectrometry with flame (FAAS) and electrothermal atomization (ETAAS) were proposed. For the separation and enrichment of chromium species a new selective sorbents - ion imprinted polymers (IIP) with imprinted chromium ions as Cr(III)-8-hydroxyquinoline, Cr(III)-1,10-phenanthroline and Cr(III)-nicotinic acid were designed and synthesized. For isolation of chromium species from solid samples appropriate extraction reagents were selected and extraction procedures were developed. The extracted chromium species were separated by ion exchange chromatography on anion-exchange column after complexing a cationic form of Cr(III) with EDTA for formation of anionic Cr(III)-EDTA<sup>-</sup> complex. The separated species were determined by inductively coupled plasma mass spectrometry with using 8800 ICP-QQQ spectrometer (Perlan Technology). For elimination of spectral interferences during determination of chromium in mobile phase the reaction cell with oxygen gas was applied. All developed methods were validated with the use of certified reference materials of wastewater RES 10.2, RES 25.2 and soil CRM041 and successfully applied for analysis of environmental samples (surface water, municipal wastewater, soil).*

*The authors kindly acknowledge the financial support from the Polish National Science Centre (DEC-2012/07/B/ST4/01581).*

## A Simple Speciation Method for Monitoring Arsenic Removal from Drinking Water

Victor G. Mihucz<sup>\*A,B</sup>, László Bencs<sup>C</sup>, Mihály Óvári<sup>D</sup>, Christina Strelí<sup>E</sup>, Gyula Záray<sup>A,B,D</sup>

<sup>A</sup>Laboratory for Environmental Chemistry and Bioanalytics, Institute of Chemistry, Eötvös Loránd University, H-1117 Budapest, Pázmány Péter stny. 1/A, Hungary; <sup>B</sup>Hungarian Satellite Centre to Trace Elements Institute for UNESCO, Institute of Chemistry, Eötvös Loránd University, H-1117 Budapest, Pázmány Péter stny. 1/A, Hungary; <sup>C</sup>Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Hungarian Academy of Sciences, H-1525 Budapest, POB 49, Hungary; <sup>D</sup>Centre for Ecological Research, Danube Research Institute, H-1113 Budapest, Karolina út 29, Hungary; <sup>E</sup>Atomintstitut, Technische Universität Wien, A-1020 Vienna Stadionallee 2, Austria

\*vgmihucz@chem.elte.hu

**ABSTRACT:** The arsenic (As) content in natural waters covers a wide range, i.e. from lower than 0.5 µg/L to more than 5000 µg/L. High-As groundwater areas have been detected in Hungary, but aquifers in Argentina, Chile, Mexico, China, West Bengal (India), Bangladesh and Vietnam are also affected by natural As contamination. In terms of the extent of the population exposure to high As concentrations, the West Bengal basin leads with more than 40 million people. On the other hand, the toxicity of As depends on its oxidation state and chemical environment. Thus inorganic As(V) and methylated As(V) species are less toxic than (in)organic As(III) species. Therefore, As speciation gives more realistic information on the exposure of the population to As than total As, although the latter is also necessary to be determined.

Conventional As speciation methods involve in high performance liquid chromatographic (HPLC) separation on ion-exchange columns followed by hyphenation to an atomic spectrometric detector most commonly nowadays, inductively coupled plasma mass spectrometry (ICP-MS). Development of alternative methods aiming at reducing the operational costs by substituting either HPLC or ICP-MS, or both has been attempted. Solid phase extraction (SPE) with cation and anion exchange cartridges seems to be reliable for on-site separation of inorganic As(III) and As(V) as well as organoarsenicals, such as dimethylarsinic acid and monomethyl arsonic acid present at low µg/L concentrations.

Water supplies in Hungary also suffer from natural As contamination, especially in the southeastern part of the country. After the accession of Hungary to the European Union (EU), Hungary had to adopt the EU/83/1998 regulation that prescribes As content in drinking water lower than 10 µg/L. Regarding this, Hungary received derogation twice, in order to give enough time for efforts to meet this strict regulation. By the end of 2016, As reduction technologies had to be implemented in all settlements with affected water supplies. In the present work, an easy method involving the use of SPE cartridges has been applied for monitoring the technological water purification processes aiming at reduction of As with potassium permanganate and iron(III) sulfate used as an oxidizing agent and a coagulant, respectively, in water works companies. After on-site separation of As(III) and As(V), the separated and acidified fractions can be easily analyzed by any powerful, but low-cost atomic spectrometric techniques, such as high-resolution continuum source graphite furnace atomic absorption spectrometry or total-reflection X-ray fluorescence spectrometry.

## **LIBS and XRF analysis of heavy metals adsorbed in fish bones: Adsorption Isotherm and Kinetics Studies**

Reham Afifi Rezk<sup>\*A</sup>

<sup>A</sup>Applied Laser Spectroscopy Group (ALS) National Institute of Laser Enhanced Sciences (NILES)  
Technological Institute (HTI) Cairo (EGYPT)

\*reham.rezzk@gmail.com

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*ABSTRACT: In the present work, the fish bones that known to have unique adsorption capacity were used for removal of heavy metals (Cu and Co) from wastewater. Sorption process exhibits a function of initial metal concentration and contact time. Laser induced breakdown spectroscopy (LIBS) as a spechthrochemical analytical technique is used for qualitative and quantitative analysis of the water samples. X-ray Fluorescence (XRF) is exploited to characterize the remediation of wastewater. Under optimized conditions, the accuracy of LIBS calibration curves is confirmed by using XRF technique. Furthermore, lower detection limits of Cu and Co were calculated, as well as, the removal efficiency percentage for Cu and Co was compared. The results assure that the removal efficiency for copper is higher than that of cobalt. The Langmuir and Freundlich isotherm models analyzed the equilibrium adsorption data. However, the pseudo-second-order kinetic model provided the best fit to the experimental data for the adsorption of heavy metals using fish bones.*

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# Application of Graphite Furnace Atomic Absorption Spectrometer with Zeeman High Frequency Polarization Modulation background correction for environmental analysis.

Nikolay Ivanov\*

Lumex Analytics GmbH Naher Str. 8 D 24558 Wakendorf II

n.ivanov@lumexanalytics.de

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*ABSTRACT: Graphite Furnace Atomic Absorption Spectrometry (GFAAS) is well known and reliable method for elemental analysis. It applies for element determination in a variety of samples, including many environmental objects (ground water, soils, sediments, etc).*

*Traditionally all environmental objects are treated by sample preparation before GFAAS measurement.*

*But any sample preparation needs time, money and exposes to the risk of sample contamination, so it is desirable to exclude or at least simplify sample preparation.*

*There are many reasons for sample preparation, one of them is desire to decrease nonselective absorbance during atomization. The problem of nonselective absorbance has at least two sides:*

- *Nonselective absorbance decrease intensity of emission and as results make analytical characteristics worse;*
  - *High dynamic nonselective absorbance may leads to some system errors in selective absorbance determination.*
- Zeeman High Frequency Polarization Modulation background correction system [1] was presented as a method devoid of system errors in a case of high dynamic nonselective absorbance. After sufficient revision of the method [2] it was realized in an atomic absorption spectrometer MGA-1000 by Lumex Instruments.*

*Results of Cd, Pb, As determination in some environmental objects are presented in the work. Features of Zeeman High Frequency Polarization Modulation background correction allow us significantly decrease and simplify sample preparation.*

## *Reference*

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# *Environment Session*

## ***Envir IV***

*(Thu. 15<sup>th</sup> of June, h. 11.15-12.45)*

## Temporal Elemental Release During Biomass Combustion Using Microwave Assisted Laser-induced Breakdown Spectroscopy

Jan Viljanen<sup>B</sup>, Md Abdul Wakil<sup>A</sup>, Juha Toivonen<sup>B</sup>, Zeyad T. Alwahabi<sup>\*A</sup>

<sup>A</sup> School of Chemical Engineering, The University of Adelaide, S.A. 5005, Australia.

<sup>B</sup> Tampere University of Technology, Laboratory of Photonics, P.O. Box 692, FI-33101 Tampere, Finland.

\*zeyad.alwahabi@adelaide.edu.au

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*ABSTRACT: In this work, microwave assisted laser-induced breakdown spectroscopy (MW-LIBS) is used to record temporal elemental release during combustion of biomass. This is also the first time Near-Field Applicator coupled MW-LIBS is presented in gas phase. The extended lifetime of laser induced plasma with increased plasma temperature enables improved analytical performance for LIBS detection of also the challenging elements, such as chlorine. New information on temporal elemental release from biomass fuels aids in power plant operation and designing to optimize the combustion process and avoid undesired side effects, i.e. slagging and fouling.*

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## Element Determination By Atmospheric-Pressure Solution Cathode Glow Discharge And Atomic Emission Spectrometry

Zheng Wang\*, Qing Li, Chuchu Huang, Jiaxian Mo, Jiaxian Ma, Rongyin Gai

Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China.

\*wangzheng@mail.sic.ac.cn

**ABSTRACT:** Atmospheric-pressure solution cathode glow discharge (SCGD) as an emerging analytical tool has attracted more and more attention attributed in the advantages of the simplexes in sensor measurement and low-cost. Moreover, recent studies show that SCGD-AES can provide detection limits (DLs) for several metals, such as lithium, sodium, or potassium, at or below the tens of parts per billion ranges [1,2]. However, SCGD systems provide heavy metals, such as Hg, Pb, and Cr, DLs higher than tens of parts per billion, which does not meet the requirements for quantifying heavy metals at very low levels, especially, in environmental and biological samples. Firstly, addition of the ionic surfactant CTAC to electrolyte solutions resulted in a decrease in dynamic surface tension, an increase in power density, and improvements in excitation efficiency, resulting in the enhanced sensitivity of SCGD-AES toward Cd, Hg, Pb, and Cr [3]. CTAC at 0.15% (mass percentage) showed maximum enhancement of emission signals. The DLs of Cd, Hg, Pb, and Cr were 1.0, 7.0, 2.0, and 42 ng·mL<sup>-1</sup>, respectively. Secondly, the simple and accurate methods of ionic mercury (Hg<sup>2+</sup>)[4], lead (Pb<sup>2+</sup>)[5] and hexavalent chromium [6] analysis in aqueous solutions based on on-line-SPE and SCGD-AES with modified mesoporous silica were developed. The use of selective mesoporous material SH-SBA-15 and mesoporous silica-grafted graphene oxide (GO-SBA-15) facilitated Hg<sup>2+</sup> and Pb<sup>2+</sup> extraction and removal in aqueous samples, respectively. Sensitive detection of Hg<sup>2+</sup> was achieved with a DL of 0.8 µg/L, and Pb<sup>2+</sup> was 0.91 µg/L, which are significantly better than the earlier study with similar SCGD-AES. The lysine-modified mesoporous silica (Fmoc-SBA-15) with good selective adsorption of Cr(VI) at pH 3. An enrichment factor of 91 was achieved under optimized experimental conditions. A FI-SCGD-AES detection limit of 0.75 µg·L<sup>-1</sup> could be achieved for Cr(VI), with a linear range of 10–10000 µg·L<sup>-1</sup>. Moreover, the high reuse times of the materials and the low-cost characteristic of the FI-SCGD-AES make the method cheap. Thirdly, a novel method of hydride generation (HG) coupled to SCGD-AES for the ultratrace determination of tin, germanium, and selenium was developed[7]. In this novel SCGD process, gas introduction was permitted using a hollow titanium tube as both the anode and sampling port. A significant improvement in both selectivity and sensitivity was achieved, which was reflected in an improvement in the detection limits (DLs) by 3 orders of magnitude, in addition to successful valence analysis of Se without the requirement for chromatographic separation. The detection limits of Sn, Ge, and Se were determined to be 0.8, 0.5, and 0.2 µg/L.

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## A hierarchical classification approach for the identification of different waste polymers by hyperspectral imaging

Giuseppe Bonifazi, Giuseppe Capobianco, Vanessa Di Giovenale, Silvia Serranti\*,

Department of Chemical Engineering, Materials & Environment, Sapienza University of Rome,  
Via Eudossiana 18, 00184 Rome, Italy.

\*silvia.serranti@uniroma1.it

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*ABSTRACT: Aim of this work is to recognize different waste polymers through an innovative strategy based on a multivariate approach and a non-invasive spectroscopic technique. Five different plastic waste samples were chosen for the investigation: polyvinyl chloride (PVC), polypropylene (PP), polystyrene (PS), high density polyethylene (HDPE) and low density polyethylene (LDPE). A calibration dataset was realized utilizing the corresponding virgin polymers. Hyperspectral imaging in the short wave infrared range (1000-2500 nm) was thus chosen to evaluate the different plastic spectral attributes finalized to perform their recognition/classification. After exploring polymer spectral differences by principal component analysis (PCA), a hierarchical PLS-DA model was built allowing to classify the five different plastic waste typologies. Finally, an interval PLSDA was applied in order to reduce the number of useful wavelengths to speed up the process without losing quality in the classification. The proposed methodology, based on hierarchical classification, is very powerful and fast, allowing to recognize the five different polymers in a single step.*

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## Automated Identification of Environmental Microplastics Based on FT-IR Spectroscopy.

Gerrit Renner<sup>\*A,B</sup>, Torsten C. Schmidt<sup>B</sup>, Marion Egelkraut-Holtus<sup>C</sup>, Jürgen Schram<sup>A</sup>

<sup>A</sup>Instrumental Analytical and Environmental Chemistry, Niederrhein University of Applied Sciences,  
Frankenring 20, D-47798 Krefeld, Germany;

<sup>B</sup>Instrumental Analytical Chemistry, University of Duisburg-Essen, Universitätsstr. 5, D-45141 Essen, Germany;

<sup>C</sup> Shimadzu Europa GmbH, Albert-Hahn-Str. 6-10, D-47269 Duisburg, Germany.

\*grenner87@gmail.com

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*Significant amounts of plastics are released into environment due to careless or unsuitable handling, which is followed by unknown consequences for our eco system. One key step, studying interactions of microplastics with the ecological system, is to identify plastics within environmental samples. In this context, Infrared (IR) spectroscopy is one of the most common and robust analytical techniques to identify and characterise synthetic polymers, as it is fast, relatively cheap and highly selective. Unfortunately, ageing processes and surface contamination especially with bio-films impede this characterization. A complex and time consuming cleaning procedure is a common solution for this problem. However, it implies an artificial change of sample composition with a risk of losing important information or even damaging microplastic particles.*

*In the present work, we introduce a new chemometric approach to identify contaminated and heavily weathered microplastics without any cleaning. The main idea is to separate characteristic from irrelevant information within an FT-IR spectrum by evaluating vibrational bands only. Regarding this, we developed an automated software application, that uses FT-IR spectra to create high characteristic fingerprints by means of vibrational band information.*

*A total of 300 unique naturally weathered micro particles were measured with FT-IR ATR and identified successfully with the new identification method. To that end, all samples were compared with a selection of common reference plastics and bio polymers. As it turns out, the accuracy of identification rises significantly from 60 % to 95 %. Our new approach can be a useful tool to compare and describe similarities of FT-IR spectra of microplastics. This may improve further research studies on this topic.*

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# *Fundamentals of LIBS Session*

## ***LIBS I***

(Mon. 12<sup>th</sup> of June, h. 9.45-10.45)



## Measurement of electron temperature and density in laser-induced hydrogen and laboratory air plasma

Christian G. Parigger<sup>\*A</sup>

<sup>A</sup>Department of Physics and Astronomy, University of Tennessee, University of Tennessee Space Institute, Center for Laser Applications, 411 B.H. Goethert Parkway, Tullahoma, TN 37388, U.S.A.

\*cparigge@tennessee.edu

**ABSTRACT:** Optical breakdown causes expansion dynamics measurable for time delays up to orders of magnitude longer than the pulse duration. In laser-induced breakdown spectroscopy (LIBS), especially when using emission spectroscopy, line-of-sight measurements of the spectral plasma distributions are recorded. Typically, averages of the micro-plasma are dispersed to cover the near UV, visible to near IR wavelength range. Figure 1 shows shadowgraphs with image dimensions of 12.7 mm  $\times$  12.7 mm, following optical breakdown in laboratory air at standard ambient temperature pressure.

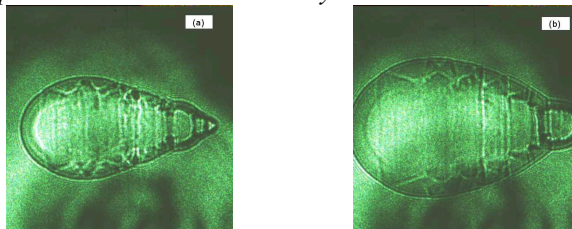


Figure 1: Images of air plasma following optical breakdown. Time delays (a)  $\tau_{(a)} = 1 \mu\text{s}$  and (b)  $\tau_{(b)} = 2 \mu\text{s}$ .

The laser-supported, expanding plasma is generated with focused 850 mJ, 6 ns, 1064 nm radiation and projected using time-delayed 532 nm, 14 ns laser pulses. The IR excitation radiation is focused from left to right. The images illustrate details including vertical stagnation layers and shock waves that show close to spherical or prolate spheroidal symmetry. Comparisons of Figs. 1 (a) and (b) indicate a maximum vertical diameter ratio of  $d_{(b)}/d_{(a)} \sim (\tau_{(b)}/\tau_{(a)})^{0.4} \sim 1.3$ , predicted by the Taylor-Sedov blast wave model. Increased electron density,  $N_e$ , and temperature,  $T_e$ , are anticipated near the outer regions, investigated with computed tomographic Abel- or Radon- inverse transforms. For optically thin plasma, spectral line shapes can be resolved along the line-of-sight. The  $N_e$  and  $T_e$  distributions are deduced from atomic line widths and ratios.

## Inter-pulse delay influence on the plasma expansion dynamics in DP-LIBS investigation of a graphite sample in vacuum

Paweł Gasior<sup>\*A,B</sup>, Monika Kubkowska<sup>A</sup>, Przemysław Tchorz<sup>A</sup>, Ewa Kowalska-Strzeciwiłk<sup>A</sup>

<sup>A</sup>IPPLM, Institute of Plasma Physics and Laser Microfusion, Warsaw, P.O. BOX 49, Hery str. 23, Poland

<sup>B</sup>Warsaw University of Technology, Institute of Electronic Systems, Nowowiejska 15/19, Warsaw, Poland.

\*pawel.gasior@ipplm.pl

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**ABSTRACT:** Although dual pulse LIBS is a well-known and accepted technique for LIBS signal enhancement and was a scope of numerous and extensive analyses, the complexity of the phenomena involved make it still interesting for fundamental research on laser plasma processes. A relatively unexplored area of research includes the behavior of the dual-pulse laser plasma in vacuum conditions in which the plasma plume expansion is not a linear function of laser pulse density or inter-pulse delay but it is governed by non-linear mechanisms. It manifest in some threshold conditions for different regimes of the plasma behavior. In the research described in this paper the carbon dual pulse laser plasma is characterized by LIBS and ion time of flight diagnostics (Electrostatic Ion Energy Analyzer, Ion Collectors). Several regimes of plasma expansion can be observed depending on the inter-pulse delay, which cannot be explained by linear combination of the ion components resulting from subsequent pulses. The influence of the non-linear phenomena also manifests in the ion energy increase and considerable plasma life time growth for given irradiation parameters. Ion groups separation is observed by LIBS and it increases flexibility in terms observation of particles of a given charge states and energy independently. The research is complemented by investigation of laser produced craters for single and dual pulse operation in dependence on the inter-pulse delay. The research attempts to explain the observed phenomena, which also facilitates understanding the processes occurring in dual pulse interactions in atmospheric conditions.

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## Use of CaF molecular emission to improve the analytical capabilities for fluorine detection by LIBS.

César Alvarez-Llamas, Raquel Álvarez García, Jorge Pisonero, Nerea Bordel

Department of Physics, University of Oviedo, Gonzalo Gutierrez Quiros s/n, Mieres (Asturias), Spain

\*bordel@uniovi.es

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**ABSTRACT:** *Spectroscopic detection of fluorine in solid samples, and in particular using Laser-Induced Breakdown Spectroscopy (LIBS), is a challenging task due to the low excitation efficiency of this element. The most common approach to fluorine analysis is the use of a Helium atmosphere to increase the signal-to-background ratio of fluorine atomic lines in the infrared spectral region (680-710 nm). Alternatively, the measurement of molecular compounds formed in the LIBS plasma might be used to indirectly detect fluorine. In this work, the detection of CaF molecular emission bands from the  $B^2\Pi - X^2\Sigma$  system is investigated to improve the analytical capabilities of atmospheric air LIBS for the determination of fluorine traces in solid samples. In a first step, it was investigated the quantification capabilities of LIBS in powdered samples with calcium content. In particular, Cu matrix samples containing different fluorine concentration (between 50 and 600  $\mu\text{g/g}$ ), and variable amounts of Ca, are used to demonstrate linear relationships between CaF emission signal and F concentration. The analysis of fluorine in calcium-free samples was also investigated, in particular the use of an external source of Ca to form the CaF molecular bands by the nebulization of a Calcium Nitrite solution over the sample surface. This process could be carried out as a sample pre-treatment in which the nebulization is independent of the LIBS analysis, or it could be simultaneous to the analysis. In addition, it has been investigated the analytical capabilities for fluorine detection in a concentration range between 50-800  $\mu\text{g/g}$  obtaining a detection limits comparable with those obtained in Ca-containing sample. Furthermore, a study of the influence of the aerosol in the laser-induced plasma, focused on the change in the plasma emission and plasma electron temperatures, has been performed.*

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# *Fundamentals of LIBS Session*

## ***LIBS II***

*(Mon. 12<sup>th</sup> of June, h. 11.15-13.00)*

## Characterization of laser-produced plasmas

Jörg Hermann\*<sup>A</sup>

<sup>A</sup>LP3, CNRS - Aix-Marseille University, Marseille, France.

\*hermann@lp3.univ-mrs.fr

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**ABSTRACT:** Plasmas have been generated by laser-matter interaction in an uncountable variety of experimental conditions. Even plasmas produced by lasers for analytical purposes were generated in a vast multiplicity of conditions, using different experimental arrangements and diverse techniques for their characterization and analytical data processing. Motivated by diversified applications and the need of measurement optimization, LIBS plasmas were generated with laser beams of various wavelengths, pulse durations, pulse energies, focusing geometries, under different background gases and pressures. In addition, double-pulse laser irradiation was applied to improve the plasma properties in the view of analytical measurements. Beside the LIBS measurements mostly performed using time-resolved spectroscopy, numerous techniques were employed to characterize the temporal and spatial evolution of laser-generated plasmas. Among these, fast imaging was applied to characterize the expansion dynamics of excited plasma species. This technique was amended by using narrow band optical filters, enabling thus the selective observation of individual plasma species. Shadowgraphy and interferometry were used to follow shock waves and electron density, respectively. Several research groups reported detailed diagnostics using time- and space-resolved optical emission spectroscopy. Moreover, efforts have been dedicated to the evaluation of self-absorption that presents one of the main difficulties in the characterization and exploration of the dense laser-produced plasmas. Thus, absorption measurements with the aid of a duplicating spherical mirror or an additional radiation source were performed. To improve the accuracy of electron density measurements via Stark broadening, the direct measurement of electron density and temperature via Thomson scattering was investigated. The in-situ characterization of LIBS plasmas was completed by the evaluation of the ablated mass via the analysis of the laser-produced craters. In addition to the experimental investigations, efforts in modeling have been dedicated to improve the understanding of the processes involved in laser ablation, plasma generation and plume expansion. This task is particularly difficult for typical LIBS conditions, when a nanosecond laser pulse generates a plasma under atmospheric pressure. As a matter of fact, there is nowadays no model that enables the accurate prediction of plasma properties and their evolution as a function of time and space for given experimental conditions. Modeling is limited to the qualitative description of the observed phenomena. Alternatively, several recent approaches ignore the initial processes of laser ablation and plasma ignition, describing only the plasma evolution in the time of interest for LIBS analysis. In the mostly applied calibration-free LIBS measurement procedures, the plasma is characterized at a given instant using the equilibrium approach. In contrast, the non-equilibrium case is aspired in some LIBS experiments on organic materials, tending to establish a correlation between the chemical bonds in the material and plasma emission spectrum. Molecular emission attracted growing interest in the past years, motivated by isotopic analysis, measurements of halogens or other hardly detectible elements, and for diagnostics of LIBS plasmas of organic materials. The aim of the present contribution is to give an overview on recent developments in the characterization of laser-produced plasmas and to point out open questions and requirements for further developments in laser-induced breakdown spectroscopy.

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## Modeling plasma heating by fs laser pulse.

Gianpiero Colonna\*, Annarita Laricchiuta, Lucia Daniela Pietanza

PLASMI Lab CNR NANOTEC, Bari, Italy;

\* gianpiero.colonna@cnr.it

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*ABSTRACT: The early stage of the plasma heated by fs laser pulse is investigated through a self-consistent model coupling the Boltzmann equation for free electrons and the collisional-radiative model of atoms and molecules. The plasma heating is described by considering the fast oscillating electric field generated by the laser pulse. The energy is transferred to the surrounding gas through electron collisions. This model allows the determination of the coupling between the radiation field and the ambient gas. The model has been applied to hydrogen plasma.*

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## Ultra compact high resolution OEM spectrometers for LIBS

Thomas P. Rasmussen\*

Ibsen Photonics A/S Ryttermarken 15-21, 3520 FarumDenmark (DK)

\*[inquiry@ibsen.com](mailto:inquiry@ibsen.com)

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*ABSTRACT: We demonstrate how transmission gratings in fused silica can be used to build ultra compact spectrometers with high resolution and throughput. When combined with our new fast and accurate digital electronics, we obtain an ideal solution for portable and other small-sized LIBS instrumentation.*

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## **LIBS system on the basis of Nd:YAG laser with multiloop cavity self-Q-switched by external plasma mirror.**

Vyacheslav Lebedev

Department of Optical Information Technologies and Materials, ITMO University, Saint-Petersburg, Russia

lebedev@oi.ifmo.ru

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***ABSTRACT:** Diode pumped passively Q-switched holographic Nd:YAG laser with a multiloop cavity affords a high quality laser beam due to the application of an output coupler in the form of a phase-conjugate mirror on gain gratings created inside the active medium. The laser equipped with such a cavity provides a pulse train energy up to 40% of the corresponding values for Fabry-Perot cavity based lasers. The loop cavity allows the adjustment of generation modes by outer optical impacts, i.e. via the reflection from a plasma mirror formed by the laser plasma of LIBS-characterized material. The application of a passive shutter with a high initial transmission in the considered optical system can provide an intensified Q-switching. LIBS system based on this advanced laser allowed us to develop a compact installation for the distinguishing of materials from the distance at least 5 m. Furthermore, a shutter-free transition to a Q-switching mode is also possible in this system. In this case the laser oscillation is provided as a pulse train with the duration adjustable via the variation of laser diode pumping current. A drawback of this mode relates to the insufficient stability of pulse train energy and time performances. A significant stabilization of these parameters is achieved in the case of LIBS-analysis of materials with a relatively low ablation energy affording the transition of laser oscillation to a self-Q-switched mode-locking regime. It was found that the application of the corresponding algorithm for plasma emission spectra processing allows an effective identification of materials even at unstable pulse train parameters. Earlier a high reliability of this algorithm based on spectrum normalization after each laser shot for automatic distinguishing of materials using LIBS technique was demonstrated within a broad range of spectrum measurement delay times at pulse repetition rates up to 30 Hz. The efficiency of the considered approach based on every spectrum normalization in order to compensate the plasma emission instability was also confirmed. In this study the automatic distinguishing of materials was achieved at the distance up to 0.45 m and an enhanced LIBS system is suggested on the basis of a laser capable of transition into a self-Q-switched mode by LIBS plume. For better understanding of self-Q-switching mechanism involving the plasma mirror the further research is required in order to obtain an adjustable, reproducible and sustainable laser operation mode.*

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## New procedure for verification of Local Thermodynamic Equilibrium (LTE) in Laser-Induced Breakdown Spectroscopy.

Ali Safi<sup>\*A</sup>, Gabriele Cristoforetti<sup>B</sup>, Stefano Legnaioli<sup>C</sup>, Vincenzo Palleschi<sup>C</sup>, S.Hassan Tavassoli<sup>A</sup>,  
Elisabetta Tognoni<sup>B</sup>

<sup>A</sup> Laser and Plasma Research Institute, Shahid Beheshti University, G. C, Evin, Tehran, Iran

<sup>B</sup> National Institute of Optics of the National Research Council (INO-CNR), Via G. Moruzzi 1, Pisa, Italy

<sup>C</sup> Applied and Laser Spectroscopy Laboratory, Institute of Chemistry of Organometallic Compounds, Research Area of National Research Council, Via G. Moruzzi, 1, Pisa, Italy

\*A\_Safi@Sbu.ac.ir

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*ABSTRACT: In LIBS technique, for the determination of plasma parameters and element concentration, the existence of Local Thermodynamic Equilibrium is crucial to describe the plasma through Saha-Eggert relation and Boltzmann-Maxwell distribution. In most of the papers, the McWhirter criterion is used to check the validity of LTE condition; this criterion provides the minimum electron density which is needed to warrant LTE in the plasma, defined as the value for which collisional depopulation rates for all electronic levels are at least ten times the radiative depopulation rates. It is worth to remind, however, that this criterion is not a sufficient condition to guarantee LTE. Conventional Boltzmann plots based on the experimental intensity of emission lines, on the other hand, can be used to assess the partial LTE of excited levels but are unable to provide information on the population of the ground level of neutral atoms and ions, which are the levels more populated and more prone to exhibit PLTE effects. In this work, we present a new experimental method to evaluate LTE in laser induced breakdown spectroscopy which is based on comparing the temperatures describing ground and excited states. While the temperature of excited states is calculated by using a conventional Boltzmann plot, the ground states temperature is obtained by introducing a modified Saha-Boltzmann plot, making use of columnar densities of ground levels calculated by quantifying self-absorption of resonance lines. Whenever the two calculated temperatures are the same, lower and higher atomic energy levels are populated according to the same Boltzmann distribution and therefore LTE condition is fulfilled. The proposed approach, making use of homogeneous plasma approximation, constitutes a rapid way to check the validity of LTE condition, without needing complicated experimental setups, in cases where self-absorption of resonant lines can be accurately measured.*

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*Fundamentals of LIBS Session*  
***LIBS III***

(Mon. 12<sup>th</sup> of June, h. 14.45-16.15)

## Analysis of aluminum alloys by CSigma laser-induced breakdown spectroscopy

Carlos Aragón<sup>\*A,B</sup>, José Antonio Aguilera<sup>A,B</sup>

<sup>A</sup>Departamento de Física, Universidad Pública de Navarra, Campus de Arrosadía, E-31006 Pamplona, Spain;

<sup>B</sup>Institute for Advanced Material (INAMAT), Public University of Navarre, Campus de Arrosadía, E-31006 Pamplona, Spain.

\*carlos.aragon@unavarra.es

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*ABSTRACT: CSigma laser-induced breakdown spectroscopy (C $\sigma$ -LIBS) is an approach for quantitative analysis by LIBS developed recently by our group and patented by the Public University of Navarre. It is based on the use of so-called C $\sigma$  graphs, which are generalized curves of growth allowing to include several lines of different elements. In this approach, conventional calibration with a wide set of standard samples is replaced with a characterization stage, in which the parameters characteristic of the plasma and the system are determined by fitting C $\sigma$  graphs obtained from spectra measured with a reduced set of standards. Once characterization has been accomplished, elemental concentrations of other samples are obtained through fitting of C $\sigma$  graphs using an arbitrary initial value of concentration. In previous works, our group has validated the method for the analysis of slags and rocks prepared as fused glass samples. In the present work, we report an experiment where C $\sigma$ -LIBS is applied to direct analysis of samples, specifically aluminum alloys having a wide range of elemental concentrations.*

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## A Comparative Study of Carbon Plasma Emission in Methane and Argon Atmosphere

Yousfi Houssyen<sup>\*A,B</sup>, Abdelli-Messaci Samira<sup>B</sup>, Ouamerali Ourida<sup>A</sup>.

<sup>A</sup>Faculty of Chemistry, University of Sciences and Technology HOUARI BOUMEDIENE (USTHB), BP 32 EL ALIA 16111 BAB EZZOUAR Algiers, Algeria;

<sup>B</sup>Division Milieux Ionisés et lasers, Centre de Développement des Technologies Avancées (CDTA), Cité du 20 août 1956 BP 17, Bab Hassen Alger, Algérie.

\*houssyenyousfi@gmail.com

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**ABSTRACT:** The interaction between laser produced plasma (LPP) and the ambient gas is largely studied by optical emission spectroscopy (OES). The latter constitutes a basic technique for laser induced breakdown spectroscopy (LIBS). In this work, carbon plasma created by a KrF excimer laser was studied under methane and argon atmosphere by OES. The time of flight (TOF) profiles of the emitting species of C, C<sup>+</sup>, C<sub>2</sub> observed in vacuum, methane and argon gas allows to differentiate the emission features of each species in each ambient gas. Furthermore, the CH radical and Ar<sup>+</sup> appeared only in methane and argon gas respectively. The TOF reveals a double peaks for C<sub>2</sub> and a triple peaks for C at 1 mbar of argon gas, but not observed in methane one. Into both gases, the spatiotemporal evolution of all plasma species as well different components of neutral carbon C and C<sub>2</sub> reveals the origin of each one. Moreover, into argon ambience, the first peak of C and C<sub>2</sub> follow the plasma expansion whereas the second peak moves backward undergoing reflected shocks. It was found using the Maxwell Boltzmann distribution function that the translational temperature is strongly affected by the nature and the pressure of ambient gas. A shock wave generating by the plasma species-gas interaction in contact interface was highlighted. Some chemical reaction could explain the formation process of C<sub>2</sub> and CH molecules are proposed and discussed.

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## Improved Detection Ability Using Collinear Long and Short DP-LIBS

Yoshihiro Deguchi<sup>\*A</sup>, Zhenzhen Wang<sup>B</sup>, Minchao Cui<sup>A,C</sup>, Yuki Fujita<sup>A</sup>, Renwei Liu<sup>A,B</sup>, Junjie Yan<sup>B</sup>

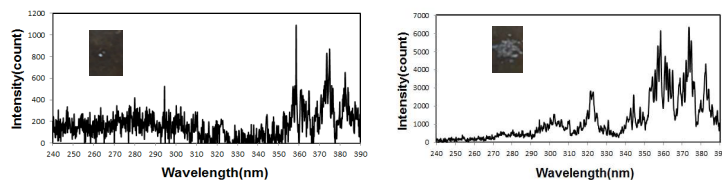
<sup>A</sup>Graduate School of Advanced Technology and Science, Tokushima University, Tokushima, Japan;

<sup>B</sup>State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an, China;

<sup>C</sup>School of Mechanical Engineering, Xi'an Jiaotong University, Xi'an, China.

\*ydeguchi@tokushima-u.ac.jp

**ABSTRACT:** DP-LIBS is an important way to enhance the emission intensities to improve LIBS analytical capability. The combinations of laser pulses with different pulse width, laser wavelength and laser power have been studied. Four geometrical configurations have been employed to realize DP-LIBS technique. A new collinear long and short DP-LIBS method was proposed to improve the detection ability and measurement accuracy by the control of the plasma cooling process using the long pulse-width laser radiation. The laser-induced plasma was generated by the short pulse-width laser and the external energy was supplied by the long pulse-width laser with the pulse width of 60  $\mu$ s(FWHM) under FR (free running) condition, which means the  $Q$  value of optical resonant cavity does not change during laser pulse formation, to sustain the plasma to improve the detection ability and feasibility in the real applications due to its collinear configuration. Simultaneously, the optical fiber delivery is easy for the long pulse-width laser radiation because peak laser intensity is low. Employing the proposed long and short DP-LIBS, the different samples of solid phase and gas phase were measured under various conditions to clarify its detection ability, as well as underwater measurement using the proposed long and short DP-LIBS. The emission intensity of signal and the signal to noise ratio can be enhanced using DP-LIBS. The plasma generated by the short pulse-width laser is stabilized and maintained at high temperature during the plasma cooling process by long pulse-width laser radiation. There are also other excellent features of this method. For example, there are the cleaning and pre-treatment effects of target surface by long pulse-width laser radiation in condition that the short pulse-width laser, which induces the plasma, is applied in the middle of the long pulse-width laser radiation, as shown in Fig.1. These results demonstrate the feasibility and detection enhancement of the collinear long and short DP-LIBS, which are applicable for solid, gas and underwater measurements.



(a) Single pulse LIBS Spectra (b) Long and short DP-LIBS Spectra

Fig.1 LIBS Spectra from rusted steel samples

## Near-Field Applicators for Efficient Microwave-Assisted Laser-Induced Breakdown Spectroscopy

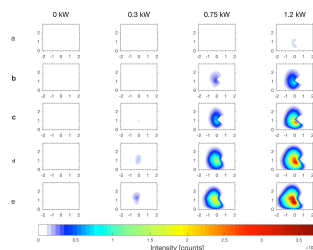
Zeyad T. Alwahabi<sup>A\*</sup>, Shengjian Jammy Chen<sup>B</sup>, Adeel Iqbal<sup>A</sup>, Christophe Fumeaux<sup>B</sup>

<sup>C</sup>School of Chemical Engineering, The University of Adelaide, S.A. 5005, Australia;

<sup>B</sup>School of Electrical and Electronic Engineering, The University of Adelaide, SA 5005, Australia

\*zeyad.alwahabi@adelaide.edu.au

**ABSTRACT:** Microwave assisted Laser induced laser induced breakdown spectroscopy has been shown enhance the detection signal to noise ratio. The type of devices needed to deliver microwave to the laser induced plasma is critically important. These devices must be able to deliver pulsed microwave radiation localized in a very small volume, typically  $\sim 2\text{mm}^3$ . There are many electromagnetic factors that must be considered to enable LIBS to benefit from sustaining the laser generated plasma with microwaves radiation and thus to enhance the elemental detection sensitivity. To evaluate a suitable NFA a series of experiments were preformed for simultaneous spectra detection and plasma imaging. This allowed us to evaluate the entire system sensitivity by monitoring the plasma spatial and temporal dimensions and by measuring the microwave-assisted signal enhancement for copper lines. Five different near field applicators were tested to evaluate the most suitable device to couple microwave radiation into the laser induced plasma. Simultaneous microwave assisted laser induced breakdown spectra were recorded targeting copper in solid samples. In addition the plasma images were simultaneously recorded for further understanding of the effect microwave power on the spatial plasma dimension. Typical examples of the plasma images are outlined in Figure 1 for five near field applicators a-e, or four microwave powers, namely 0, 0.3, 0.75 and 1.2kWatt. The plasma images, averaged for 100 laser shots, recorder using a 633 nm long-pass filter by microwave-assisted LIBS in a copper bearing mineral ore solid sample. The laser energy was 2.6 mJ. We demonstrate that by using a well-designed and tuned near field applicators, a significant boost in the signal of the copper line 324.754 nm with a factor of 849 is possible. Furthermore, an outstanding signal to noise ratio of 166 was recorded in a solid sample containing a certified 3.38 ppm copper concentration.



**Fig. 1:** Enhanced plasma images for the five different types of NFAs, a-e. The microwave power and pulse duration were 1.2 kW and 800 ms, respectively. The camera gate-width and the gate-delay were 800 ms and 1 ms respectively.



## Effect of Laser Pulse Energy and Delay Time in Double-Pulse on laser ablation and Plasma Radiation: Modeling and Numerical Simulation

Yaser Nosrati Ghods \*, Seyed Hassan Tavassoli

Institute of Laser and Plasma Research , University of Shahid Beheshti, Evin, Tehran, Iran.

\*ya\_nosrati@sbu.ac.ir

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*ABSTRACT: In this paper, laser ablation and plasma radiation for single pulse and double pulse Laser Induced Breakdown Spectroscopy is modeled and simulated. The rate of ablation and the mechanism of ablation for Copper element in presence of Helium background gas at 1 atm pressure for several conditions are compared. Double pulse with different inter-pulse delay times and laser pulse energies are used to interact with sample and its effect on rate of ablation and plasma radiation was studied. Our results reveal that ablation rate in double pulse scheme is more than single pulse. Ablation profile is smoother than single pulse and also the optimized interval time between pulses is determined. It is being noted that our results show that this model is in good agreement with experimental result. Heat conduction equations in the target and also plasma expansion dynamics in the plume are solved. At the interface between the target and the vapor, Knudsen layer, equations of energy and mass are coupled. In addition, Saha–Eggert equations are used to investigate plasma formation. Effects of excitation energy on plasma expansion and its emissivity are studied. Moreover, the influence of plasma shielding, due to photoionization and inverse bremsstrahlung processes is considered. Continuous radiation, Bremsstrahlung and blackbody radiation, and spectral emissions of the plasma are also examined. The results show that in the double pulse scheme, continuous radiation decrease much earlier than the single pulse. Also, it is observed that FWHM in the double pulse is narrower than single pulse.*

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*Fundamentals of LIBS Session*  
***LIBS IV***

(Tue. 15<sup>th</sup> of June, h. 9.15-10.45)

## Model of Stimulated Emission in Aluminum Laser-Induced Plasma Produced by Resonance Pumping

Igor Gornushkin<sup>\*A</sup>, Alexander Kazakov<sup>B</sup>, Reto Glaus<sup>A</sup>, Lev Nagli<sup>C</sup>, Ulrich Panne<sup>A</sup>

<sup>A</sup>BAM Federal Institute for Materials Research and Testing, Richard-Willstätter-Str. 11, 12489 Berlin, Germany; <sup>B</sup>St. Petersburg State University of Technology and Design, B. Morskaya 18, 191186 S.-Petersburg, Russia; <sup>C</sup>Ariel University, Physics Department, Ariel 40700, Israel

\*igor.gornushkin@bam.de

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**ABSTRACT:** Stimulated emission observed experimentally in aluminum laser induced plasma is modeled via a kinetic approach. The simulated emission at several cascade transitions is created by a pump laser guided through the plasma at several microseconds after its creation and tuned in resonance with the strong transition at 266 nm. A two-dimensional space-time collisional radiative plasma model explains the creation of the population inversion and lasing at wavelengths 2.1  $\mu$  and 396.1 nm. The population inversion for lasing at 2.1  $\mu$  is created by depopulation of the ground state and population of the upper state via absorption of resonant radiation at 266 nm. The population inversion for lasing at 396.1 nm occurs during the laser pulse via the decay of the population of the pumped upper state to the lasing state via cascade transitions driven optically and by collisions. The model predicts that the population inversion and corresponding gain may reach high values even at moderate pump energies of several  $\mu$ J per pulse. The efficiency of lasing at 2.1  $\mu$  and 396.1 nm is estimated to be on the order of a percent of laser pump energy. The polarization effect that the pump radiation at 266 nm imposes on the stimulated emission at 396.1 nm is discussed. The calculated results are favorably compared to experiment.

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## Wavelength Dependence of Surface Transformations in Femtosecond Laser Ablation of Metallic Thin-Films.

I. M. Carrasco-García, J. M. Vadillo, J. Laserna.

Department of Analytical Chemistry, University of Málaga, Málaga, Spain.

laserna@uma.es

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**ABSTRACT:** *The temporal gap between the reaching of the laser photons onto the sample surface and the production of a plasma is a key characteristic of femtosecond laser ablation. Such absence of laser-plasma interaction in the femtosecond regime opens a time window of several hundred of picoseconds to visualize the very early stages of laser ablation without the disturbance of plasma shielding, and in the real possibility of describing the timeline of the alterations of the sample surface with a time resolution limited by the detection system.*

*Pump-probe time-resolved microscopy using femtosecond pulses has demonstrated a high reliability and reproducibility in monitoring the concerned surface alterations, with a temporal resolution only limited by the laser pulse width. This technique showed that an interference phenomenon called Dynamic Newton's Rings is related to the shape of the ablation front by the number and width of observed rings. Since the laser wavelength plays an important role in the involved phenomena, it is of interest to study the temporal evolution of the surface as a function of the laser wavelength. The present study used a Ti:Sa laser providing 35 fs pulses, and a fundamental wavelength centered at 800 nm. Laser pulses run through a harmonic generator, which supplies the second and third harmonics of the pump beam. For the experiment, several pump-probe configurations have been used to study separately the effect of the laser pump wavelength and to reveal its implication on the ablation process. The results demonstrate that, after the arrival of the pump laser and prior to the onset of sample ablation, the surface evolves faster with beams of larger photon energy, as it has been observed by an earlier generation of Newton's Rings at 266 nm and 400 nm at delays of 300 approximately, whereas at 800 nm under the same conditions of energy were not observed until delays of 900 ps.*

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## Reactive molecular dynamic simulations to investigate molecular formation in laser-induced plasmas

Thomas Dietz, Marcell Wolnitz, Peter Kohns, Georg Ankerhold\*

University of Applied Sciences Koblenz, RheinAhrCampus, Joseph-Rovan-Allee 2, 53424 Remagen, Germany

\*[ankerhold@hs-koblenz.de](mailto:ankerhold@hs-koblenz.de)

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**ABSTRACT:** The formation of diatomic molecules or radicals in the cooling phase of a laser-induced plasma is mainly determined by thermodynamical parameters as the local plasma temperature, pressure and particle density. We adapted the well-known method ReaxFF [1] to simulate the generation of molecular bonds in our time-resolving LIBS experiments.

Instead of standard quantum mechanical or continuous simulation methods [2], ReaxFF uses a hybrid form based on the calculation of the bond order. The main advantage is the short computation time of molecular bonds compared to standard approaches. For several elements the specific parameters of the atomic force-fields are provided by Adri van Duin from Caltech University. This allows the simulation of molecular formation at a fixed thermodynamic equilibrium as well as ramp simulations to reveal temperature dependent molecular concentration profiles. Our molecular simulations allow to explain the observed molecular band emission, to investigate molecular interferences with other elements in the sample, and to determine the parameters of LIBS experiments in order to obtain high molecular band emission rates.

As an application, we simulated the temporal behavior of molecular and radical species of CaO and CaCl to explain the observed molecular band emission of chloride-contaminated concrete. Quantitative LIBS measurements can help to determine the chloride content of buildings such as bridges or parking garages [3]. Their stability is drastically reduced by the diffusion of chloride from de-icing salt into the concrete. Corrosion of the steel reinforcement occurs if the chloride contamination exceeds a certain level.

**Acknowledgments:** This project is supported by the German Federal Ministry for Economic Affairs and Energy (BMWi), ZIM project grant No KF26821030F4. We thank Adri van Duin from Caltech University for providing specific force field parameters.

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  - <sup>2</sup> S.V. Shabanov, I.B. Gornushkin, "Anions in laser-induced plasmas", *Appl. Phys. A* 122.7, 1-24 (2016)
  - <sup>3</sup> A.-S. Rother, T. Dietz, P. Kohns, G. Ankerhold, "Molecular laser-induced breakdown spectroscopy for elemental analysis –A new approach to an advanced material research", *Technisches Messen tm*, vol. 84, no. 1, 23-31 (2017) (DOI 10.1515/teme-2016-0032)
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## Determination of Detection Limits of Trace Elements in Aluminium Using Stagnation Layers.

B. Delaney,<sup>\*A</sup> P. Colley,<sup>B</sup> T.J. Kelly,<sup>A</sup> E.T. Kennedy,<sup>A</sup> J.T. Costello<sup>A</sup>

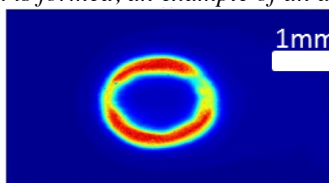
<sup>A</sup>School of Physical Sciences and the National Centre for Plasma Science and Technology (NCPST),  
Dublin City University, Glasnevin, Dublin 9, Ireland;

<sup>B</sup>College of Engineering, University of Notre Dame, Notre Dame, IN 46556, United States.

\*ben.delaney5@mail.dcu.ie

**ABSTRACT:** When two laser plasmas are formed adjacent to each other, in an ambient pressure of less than  $10^{-1}$  mbar, the plasmas will expand not normal to the target but also laterally. The plasmas will decelerate at the collision plane, with their kinetic energy being converted into excitation energy, forming what is known as a stagnation layer while the two initial plasmas are known as 'seed plasmas'<sup>1</sup>.

Current interest in stagnation layers comes from the ability to manipulate their physical characteristics; density, temperature, shape, etc. by varying target geometry or laser-target interaction characteristics<sup>2-3</sup>. The traditional set up for generating stagnation layers involves using a wedge prism to split a laser beam into two parts; these beams are then focused onto the target with a lens. This system while useful for quickly and easily generating stagnation layers does have some drawbacks, principally the inherent asymmetry of the set up. When the upper half of the laser beam is passed over the wedge prism the lower half passes through the prism and is deflected downwards. The deflected beam gives rise to a focal spot with a somewhat elliptical footprint and consequently a seed plasma with potentially different characteristics than the one formed by the undeflected portion of the laser beam. Hence the resulting stagnation layer which can also become asymmetrical. To generate a symmetrical stagnation layer the wedge prism in the above set up was replaced with an axicon which can be either a plano-conical lens or a rotationally symmetric prism<sup>4-5</sup>. A Gaussian laser beam, passed through an axicon, is first transformed into a Bessel-Gauss beam, when passed through a plano-convex lens an annular beam profile is formed at the focal plane of the lens. When a target is placed in the focal plane of the lens an annular plasma is formed, an example of an annular plasma is shown in figure 1.



**Figure 1.** Time resolved broadband emission imaging of a copper plasma with a 5ns exposure time taken 5ns after plasma formation.

Time-resolved broadband emission imaging has been employed to investigate the evolution of an annular laser produced plasma. To date it has been shown that a stagnation layer forms at the centre of an annular copper plasma formed at an ambient pressure below  $1 \times 10^{-3}$  mbar. A comparison between the limit of detection of a traditional LIBS set up, a dual seed plasma stagnation layer LIBS set up and an annular plasma stagnation layer LIBS set up will be drawn. The results of these comparisons will be presented at the conference.

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2. Luna H., Kavanagh K.D. Costello J.T., *Journal of Applied Physics*, 2007, 101, 3, 033302-1
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## A new interactive interface to the NIST Atomic Spectra Database for LIBS spectra simulation and diagnostics

Alexander Kramida\*, Karen Olsen, Yuri Ralchenko

National Institute of Standards and Technology, Gaithersburg, MD, USA.

\*alexander.kramida@nist.gov

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*ABSTRACT: The fundamental atomic data necessary for modeling and diagnostics of plasma pertinent to laser-induced breakdown spectroscopy (LIBS), i.e., energy levels and radiative transition probabilities, are already available for many years in the Atomic Spectra Database (ASD) of the National Institute of Standards and Technology (NIST). For about a decade, the ASD interface offers a limited capability to produce simulated spectra in the form of Saha-Boltzmann plots. To better address the needs of the LIBS community, we developed a new user-friendly interface to the critically evaluated atomic data in ASD that allows generation of LIBS spectra in arbitrary plasmas. With this interface, it is easy to specify a plasma composition and rough initial estimates of observational parameters, such as electron temperature and density, wavelength range, and spectral resolution. Initial Saha-Boltzmann modeling is made on the server side, and all relevant data, such as spectral lines and energy levels data are transmitted to the user's computer, which plots the simulated spectrum. Then it is possible for the user to change the appearance of the plot by zooming in and out or selecting graphs for individual species and recalculate the simulated spectrum with modified parameters. In addition, the user can load an experimental spectrum into the same plot and compare it with the simulation. In the first version, which is planned to be released in mid-2017, fitting of the experimental spectrum can be made only manually, by changing the temperature, density, resolution, or element concentrations. Future plans include an automated fitting procedure.*

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# *Geological Applications Session*

## ***Geo I***

*(Mon. 12<sup>th</sup> of June, h. 14.45-16.15)*

## **LIBS in the Earth Sciences – Recent Applications and Current Perspectives.**

Russell S. Harmon\*

Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University,  
Raleigh, NC 27695, USA

\*rsharmon@ncsu.edu

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*ABSTRACT: Since its beginnings in the mid-1960s until recently, LIBS was a laboratory-based research technique. But today, multiple commercial instrument manufacturers are offering field-portable LIBS systems, with detection limits in the  $\mu\text{g/g}$  range or better for certain elements. Software control of the analytical process, together with on-board signal processing, have automated the entire analytical process and facilitated applications like surface mapping and depth profiling. Quantitative analysis is possible based upon empirical calibration curves derived from matrix-matched standards. Geo-material identification and source determination can be readily achieved using chemometric analysis that compares acquired LIBS spectra against a pre-assembled spectral library. Thus, the time has now arrived where LIBS analysis can be readily undertaken in the field, with analytical results generated in real time. Expecting application of field-portable LIBS to be widely applied and then discussed at future LIBS conferences, this presentation reviews important recent LIBS studies of geological materials and highlights some of the current geological research being undertaken within the LIBS community. Such applications range from simple elemental/material identification and quantitative analysis of specific elements in various geological matrices to mineral and rock provenance determination, stratigraphic correlation, isotopic analysis, and standoff analysis on the surface of Mars by the ChemCam analytical system on the Curiosity rover.*

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## Lithium Brine Analysis to PPM Levels using Hand Held LIBS

David R. Day

SciAps, 2 Constitution Way, Woburn, MA, 01921, USA

[dday@sciaps.com](mailto:dday@sciaps.com)

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*ABSTRACT: Lithium mining is becoming increasingly important as the usage of lithium ion batteries continues to grow worldwide. Lithium extraction from saline groundwater brine deposits have now become a larger lithium source than hard rock mining. There is a critical need for a quick and simple analysis method for both the raw groundwater during exploration as well as during the lithium concentration process as the water is evaporated. In this paper we investigate brine solutions, which typically contain 5% NaCl, that range in lithium concentration from 0 to several thousand ppm. A technique will be described that utilizes LIBS emissions from plasmas created directly on the water surface. The advantage of this method is that there is no requirement for any drying or extraction. LOD's of less than 10ppm have been realized for which supporting data will be presented. Additionally, calibration and validation results over a large concentration range will be reviewed.*

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## Non-Invasive Elemental Analysis of Gemstones by Nano Particle Enhanced Laser Induced Breakdown Spectroscopy.

Rim Alrifai\*<sup>A</sup>, Can Koral<sup>A</sup>, Marcella Dell'Aglio<sup>B</sup>, Marco Torelli<sup>C</sup> Alessandro De Giacomo<sup>A,B</sup>

<sup>A</sup>Department of Chemistry, University of Bari, Bari 70126, Italy;

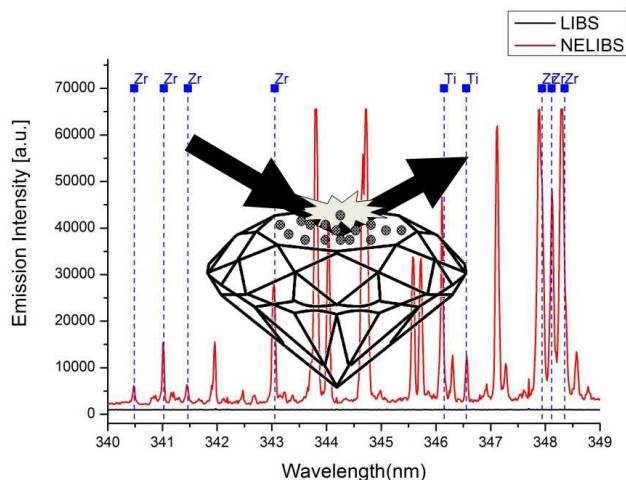
<sup>B</sup>CNR-IMIP sec Bari, Bari, 70126, Italy.

<sup>C</sup>Masterstones, Centro Analisi Gemmologiche, Via Alessandri 6A, 00151 Roma, Italy

\* rim.alrifai@uniba.it

**ABSTRACT:** LIBS analysis into transparent samples and glasses has been widely investigated in the literature. LIBS analysis of non-absorbing substrates and transparent samples stems from irreversible damages like micro cracks and the fracturing of the material. In high reflective index targets the penetration of the laser radiation into the sample following multi time internal reflections leads to macro sized cracks. This drawback limits the applicability of the LIBS technique for the precious samples like gemstones or ancient glasses. In this work we propose a variation of Nanoparticle Enhanced LIBS (NELIBS)[1] as a new approach to use the NPs deposition technique to mediate the laser and material interaction such that the breakdown of the particles deposited on the surface prevent the laser to penetrate into the transparent medium. The explosion of the NPs deposited on the surface of the sample transports the elements of the target material into the plasma phase. That superficial ablation on the target surface creates only Nano-sized damages on the sample surface which are only detectable with electron microscope. This new variation of the NELIBS approach enables the non-invasive qualitative and quantitative analysis of delicate transparent materials, including cut and polished gems and archaeological samples.

[1] A. De Giacomo, C. Koral, G. Valenza, R. Gaudiuso, M. Dell'Aglio, Perspective on the use of nanoparticles to improve LIBS analytical performance: Nanoparticle enhanced laser induced breakdown spectroscopy (NELIBS), J. Anal. At. Spectrom. 31 (2016) 1566-1573.



## Quantification of Fe/Mn ratio in iron-manganese nodules by CF-LIBS

Timur F. Akhmetzhanov\*, Andrey M. Popov, Sergey M. Zaytsev, Timur A. Labutin

Department of Chemistry, Lomonosov Moscow State University, 119234, Leninskie Gory, 1-3, Moscow, Russia

\*mozgoglot@yandex.ru

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**ABSTRACT:** Since the knowledge of heavy metal concentrations allows the decision of several scientific tasks in oceanology, the study of slurries and sediments is of great importance in oceanological research. Here some of the abovementioned tasks should be listed: (i) description of geochemistry of the oceanic sedimentary process that allows one to create geochemical model of the modern ocean; (ii) development of a basis for comparative lithological study for modern and ancient oceanic sedimentary formations; (iii) creation of a general scheme for the ore formation in the ocean since new mineral deposits are one of the criteria by which one can judge about the features of a particular type of lithogenesis; (iv) monitoring the amount of trace elements because many of them are of interest to their industrial mining (for example, rare-earth elements). The main markers to search for ore deposits within pelagic sediments are often the ratios of main components, e.g. the ratio of iron to manganese in iron-manganese nodules (IMN) samples. This value is used to determine the age of the sample that is related to its price as time accumulates rare-earth metals in the nodules. Determination is complicated by at least two factors: strong matrix effects and the lack of suitable reference samples for reliable calibration. Therefore in present work the analysis of nodule samples has been performed by calibration-free LIBS technique (CF-LIBS). In order to determine detector's delay (2.5  $\mu$ s) and gate (0.25  $\mu$ s) corresponding to local thermodynamic equilibrium, the study of plasma evolution was carried out: plasma temperature was determined by the two lines method (Mn I lines at 447.28 nm and 447.93 nm), and electron density was calculated using Stark broadening parameters of Fe I lines at 517.15 nm. A pulsed laser with a repetition rate of 5 Hz and an energy of 45 mJ/pulse has been used in the experiment. The emission of plume has been projected onto a slit of high-aperture Czerny-Turner spectrometer («HR 320» (ISA, USA) resolution of 45 000 at 400 nm and 120 000 at 520 nm) through the optical fiber. The possibility of semi-quantitative determination of basic components ratio in iron-manganese nodules samples by calibration-free LIBS has been demonstrated: the ratio has varied from 0.2 to 4.2. Comparison between external standard method and CF-LIBS has been performed, and the advantages for CF-LIBS technique have been established.

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## Accuracy and precision improvement of Laser Induced Breakdown Spectroscopy (LIBS) by geostandards

S. Pagnotta<sup>A</sup>, S. Raneri<sup>B</sup>, M. Lezzerini<sup>B</sup>, M. Tamponi<sup>B</sup>, B. Campanella<sup>A</sup>, E. Grifoni<sup>A</sup>, S. Legnaioli<sup>A</sup>, G. Lorenzetti<sup>A</sup>, F. Poggialini<sup>A</sup>, V. Palleschi<sup>A</sup>

<sup>A</sup>Applied and Laser Spectroscopy Laboratory, Institute of Chemistry of Organometallic Compounds,  
Research Area of National Research Council, Via G. Moruzzi, 1 – 56124 Pisa, Italy

<sup>B</sup>Department of Earth Sciences, University of Pisa, Via Santa Maria, 53 – 56126 Pisa, Italy

*stefanopagnotta@yahoo.it*

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*ABSTRACT: Compared to other atomic emission spectroscopy techniques, Laser Induced Breakdown Spectroscopy (LIBS) leads numerous advantages, as well as uncertainties in the measurements of elemental composition and elemental concentrations in a samples, mainly due to fluctuations in laser energy and laser-sample interaction. As a matter of fact, precision and accuracy improvements are currently promised by appropriate measurement routines (i.e.: repeated measurements and averaging of spectra) or by data processing [1]. Taking advantage from standardization routines applied for quantitative measurements in other techniques, such as X-ray spectroscopy, the main aim of this research is to evaluate the precision and the accuracy of LIBS by analyzing a selection of geostandards [2] consisting in powders of rocks and minerals which provenance, elemental composition and concentration is well known. The comparison between geostandard and LIBS measurement has allowed discussing about the precision and accuracy of the method in geological samples analysis.*

[1] Wang, Z., Li, L., West, L., Li, Z., Ni, W (2012) A spectrum standardization approach for laser-induced breakdown spectroscopy measurements, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 68, 58-64

[2] Govindaraju, K. (1994), 1994 compilation of working values and sample description for 383 geostandards. *Geostandards Newsletter*, 18: 1–158

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# *Geological Applications Session*

## ***Geo II***

*(Tue. 13<sup>th</sup> of June, h. 9.15-10.45)*



## Classification of sulfur minerals in vacuum ultraviolet and near-infrared spectral region.

Tuomo Niilahti<sup>A</sup>, Heikki Häkkänen<sup>B</sup>, Sari Romppanen<sup>A</sup>, Saara Kaski\*<sup>A</sup>

<sup>A</sup>Department of Chemistry, P.O.BOX 35 FI-40014 University of Jyväskylä, Finland;

<sup>B</sup>Department of Biological and Environmental Science, P.O.BOX 35 FI-40014 University of Jyväskylä, Finland.

\*saara.kaski@jyu.fi

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*ABSTRACT: We have used laser-induced breakdown spectroscopy (LIBS) to classify sulfur minerals. Previously the spectral region between 180 and 220 nm has been utilized to separate the economically important minerals e.g. sphalerite (ZnS) and chalcopyrite (CuFeS<sub>2</sub>). The VUV spectra have been obtained from the drill core samples in ambient air, using nitrogen purged spectrograph and high quality quartz fiber. Since this setup is hard to modify for the mine conditions, current project utilizes near-infrared detection, which is easier to customize for the remote measurements. The potential of NIR-LIBS (800 – 1300 nm) as a fast mineral identification technique for the differentiation of the ore and gangue minerals has been studied and results have been compared with simultaneous VUV-LIBS measurements. Maps of the mineral distributions have been constructed based on the chemometrics. Obtained estimations of the contents of the different mineral species could be further used for the optimal beneficiation of excavated material and the optimization of the enrichment processes. Especially the information about the contents of the sulfur containing by-products, like the most common sulfide mineral pyrite (FeS<sub>2</sub>), in the rocks is important, as its oxidation can lead to environmentally hazardous acid mine drainage.*

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## Analysis of Columbite-Tantalite Using Handheld LIBS.

Michael A. Wise<sup>A</sup>, Richard R. Hark<sup>B</sup>, Russell S. Harmon<sup>C</sup>, Chandra S. Throckmorton<sup>D</sup>,  
Andrew M. Somers<sup>E</sup>, and Leslie M. Collins<sup>D</sup>

<sup>A</sup>Smithsonian Institution, National Museum of Natural History, Washington, DC 20560

<sup>B</sup>Department of Chemistry, Juniata College, Huntingdon, PA 16652, USA

<sup>C</sup>Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC 27695, USA

<sup>D</sup>Department of Electrical and Computer Engineering, Duke University, Durham, NC 27708, USA

<sup>E</sup>SciAps, Inc., 2 Constitution Way, Woburn, MA 01801, USA

wisem@si.edu>

**ABSTRACT:** A successful pilot study of a columbite–tantalite suite from North America by Harmon *et al.* [1] and Hark *et al.* [2] that used a laboratory LIBS system resulted in correct place-level geographic classification at success rates above 90%. In this current study, we used a handheld LIBS system to analyze in real time, a set of columbite-tantalite samples from Lithium-Cesium-Tantalum-enriched granitic pegmatites from Connecticut and California (USA). The hand-held LIBS system has the advantage of rapid analyses of unprepared samples, but also can successfully identify the presence of light elements (e.g. Li & Be) which currently is not possible with any other portable instrument.

In general, our LIBS data indicates that the composition of columbite-tantalite from California is uniquely different from that of Connecticut. A PCA scores plot for all spectra collected from our samples reveals that classes are best defined by differences in Fe and Mn content regardless of their provenance. Chemical heterogeneity among samples from the same pegmatite was easily recognized. These results reinforce the idea that a handheld LIBS system has the potential for in situ field analysis of a broad range of elements in real-time and can be a useful tool in the assessment of chemical variation in columbite–tantalite from regionally different granitic pegmatites.

[1] Harmon, R. S., Shughrue, K. M., Remus, J. J., Wise, M. A., East, L. J., & Hark, R. R. (2011). Can the provenance of the conflict minerals columbite and tantalite be ascertained by laser-induced breakdown spectroscopy?. *Analytical and Bioanalytical Chemistry*, 400(10), 3377-3382.

[2] Hark, R. R., Remus, J. J., East, L. J., Harmon, R. S., Wise, M. A., Tansi, B. M., Shughrue, K. M., K. S. Dunsin, & Liu, C. (2012). Geographical analysis of “conflict minerals” utilizing laser-induced breakdown spectroscopy. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 74, 131-136.

## Three-dimensional compositional mapping of limestone by double-pulse micro-laser-induced breakdown spectroscopy.

Giorgio S. Senesi<sup>A</sup>, Beatrice Campanella<sup>B</sup>, Emanuela Grifoni<sup>B</sup>, Stefano Legnaioli<sup>B</sup>, Giulia Lorenzetti<sup>B</sup>, Stefano Pagnotta<sup>B</sup>, Francesco Poggialini<sup>B</sup>, Vincenzo Palleschi<sup>B</sup>, Olga De Pascale<sup>A</sup>

<sup>A</sup>CNR – Istituto di Nanotecnologia (NANOTEC) – PLasMI Lab, Via Amendola 122/D, 70126 Bari (ITALY)

<sup>B</sup>Applied and Laser Spectroscopy Laboratory, Institute of Chemistry of Organometallic Compounds, Research Area of National Research Council, Via G. Moruzzi, 1 – 56124 Pisa (ITALY)

giorgio.senesi@nanotec.cnr.it

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**ABSTRACT:** The composition, shape, and distribution of minerals in a rock depend mostly on its formation mechanisms and environment. Thus, the spatial distribution and chemical composition of minerals in a rock are very important to understand its textural development and history. Electron-probe microanalysis (EPMA) and micro-x-ray fluorescence ( $\mu$ XRF) are generally used to analyze geological samples and to obtain X-ray compositional mapping. The EPMA features an image and analytical spatial resolution greater than  $\mu$ XRF, especially when coupled with energy-dispersive spectrometry (EDS). However, samples to be analyzed by EPMA must be flat, polished and require carbon coating, thus mapping of large samples involve a number of sample preparation and acquisition issues. Further, an important operational mode allows to obtain the composition of samples at different depths, i.e. tomographic or 3D compositional information. The present work aims to introduce a new technique for studying the alteration conditions of a limestone sample collected from a quoin of the external wall of the Castello Svevo, Bari, exposed for decades to urban environment. The approach combines a microscale three dimensional compositional mapping with the analysis of sample. The technique is based on double-pulse micro-laser-induced breakdown spectroscopy (DP- $\mu$ LIBS) in conjunction with optical microscopy. The compositional mapping is obtained by scanning the laser beam across the rock sample surface, while the in-depth analysis (several microns) is performed by impinging multiple laser pulses on the same sample point. A chemical imaging technique is able to analyze the surface composition and discriminate adjacent layers of the sample in relation to surface sensitivity and lateral and depth resolutions which are generally defined by sampling depth, area and shape of each individual analysis, and which define the application niche of each surface analytical technique. The DP- $\mu$ LIBS technique shows to be very effective for high-resolution and fast 3D compositional mapping of the limestone rock studied, showing also a good sensitivity to sample surface roughness. Further, the technique can be applied to the analysis of any rock sample, devoid of any treatment, and is able to detect elements of low atomic weight not suffering from limitations involved with the use of standard techniques such as EPMA,  $\mu$ XRF, LA-ICP-MS. Finally, the mapping approach introduced here may represent an important and very competitive tool in future studies, also for investigating altered rock samples of different origin and nature.

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## Improving Sulfur Detection in Martian Targets with time-resolved LIBS

Susanne Schröder<sup>\*A,B</sup>, Kristin Rammelkamp<sup>A</sup>, David Vogt<sup>A</sup>, Agnes Cousin<sup>B</sup>, Olivier Forni<sup>B</sup>, Sylvestre Maurice<sup>B</sup>, Samuel Clegg<sup>C</sup>, Roger Wiens<sup>C</sup>, Heinz-Wilhelm Hübers<sup>A</sup>

<sup>A</sup>Institute of Optical Sensor Systems, German Aerospace Center (DLR), Berlin, Germany;

<sup>B</sup>Institut de Recherche en Astrophysique et Planétologie (IRAP), Toulouse, France;

<sup>C</sup>Los Alamos National Laboratory, Science Division, Los Alamos, NM, USA.

\*Susanne.Schroeder [at] dlr.de

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**ABSTRACT:** The first extraterrestrially employed LIBS instrument is ChemCam on NASA's Mars rover Curiosity, which has been successfully analyzing materials on the martian surface since the rover's landing in August 2012 [1,2]. The success of ChemCam has led to the selection of the SuperCam instrument [3] for NASA's upcoming Mars2020 rover mission. As for ChemCam, SuperCam will have a LIBS telescopic system combined with a high-resolution color remote micro-imager camera [4] for remote analysis, along with the added capabilities of complementary Raman spectroscopy, time-resolved fluorescence spectroscopy, and visible and infrared reflectance spectroscopy [5,6]. Time-resolved Raman spectroscopy will be done with the same spectrometer and detector that are used for the third wavelength range for LIBS, providing the possibility of also recording time-resolved LIBS data in a wavelength range of 536 – 853 nm. The detection of S in ChemCam data, which falls in this range, is challenging, in particular when samples with high Fe are analyzed. As the S emission is ionic and the superimposed Fe lines are mainly neutral, their emission occurs in different temporal regimes, which can be utilized for their differentiation with time-resolved LIBS. Here, we present studies on Fe-Sulfate, Pyrite, and Pyrrhotite measured in martian atmospheric conditions where we explore the S and Fe typical emission behaviors and develop strategies for improved S detection in martian targets. All data was taken at the LIBS set-up at DLR Berlin in simulated martian atmospheric conditions (7 mbar) with a high resolution (14-96 pm) Echelle spectrometer (Aryelle Butterfly, LTB Berlin) covering continuously 270-850 nm with an intensified CCD and a Nd:YAG laser (1064 nm, 8 ns, 10 Hz).

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**References:** [1] Maurice et al. (2012) Space Sci. Rev., 170. [2] Wiens, R. C. et al. (2012) Space Sci. Rev., 170. [3] Wiens et al. (2015) AGU Fall Meeting, Abstract #P51E-05. [4] Gasnault et al. (2015) LPSC, Abstract #2990. [5] Clegg et al. (2015) LPSC, Abstract #1832. [6] Fouchet et al. (2015) LPSC, Abstract #1736.

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## Laser Induced Breakdown Spectroscopy (LIBS) for gemological testing: the case of corundum gems

Germana Barone<sup>A</sup>, Paolo Mazzoleni<sup>A</sup>, Simona Raneri<sup>B\*</sup>, Marco Lezzerini<sup>B</sup>, Beatrice Campanella<sup>C</sup>,  
Emanuela Grifoni<sup>C</sup>, Stefano Legnaioli<sup>C</sup>, Giulia Lorenzetti<sup>C</sup>, Stefano Pagnotta<sup>C</sup>, Francesco Poggialini<sup>C</sup>,  
Vincenzo Palleschi<sup>C</sup>, Ugo Longobardo<sup>D</sup>

<sup>A</sup>Department of Biological, Geological and Environmental Sciences, University of Catania,  
C.so Italia, 57 - 95129 Catania, Italy

<sup>B</sup>Department of Earth Sciences, University of Pisa, Via Santa Maria, 53 – 56126 Pisa, Italy;

<sup>C</sup>Applied and Laser Spectroscopy Laboratory, Institute of Chemistry of Organometallic Compounds,  
Research Area of National Research Council, Via G. Moruzzi, 1 – 56124 Pisa, Italy

<sup>D</sup>Jeweler, Catania.

\* simona.raneri@unipi.it

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**ABSTRACT:** *In gem testing routine, one of the main requirements is to obtain the maximum amount of information without sample preparation. Even the classical gemological methods allow usually identifying the mineralogical identity of a gem, the possibility to inspect aspects as provenance of natural gemstone, and invasive and blind treatments often require the application of more sophisticated methods able to give back quantitative information [1]. Moreover, due to the development of more and more refined synthesis method, the discrimination between natural and synthetic gems is not trivial. Among gemstone analysis techniques, Laser Induced Breakdown Spectroscopy (LIBS) is increasingly worth considering; the method, already tested for example in origin determination of emeralds [2] or detection of Be-diffusion treatment in corundum [3], provides rapid results on trace-element contents, the latter considered a fingerprint of a gem. Moreover, determining a minimal damaging (an ablation area of just few micrometers), it can be extensively used on both cut and raw gemstones. In this prospective, the present paper intends to contribute the researches in gems analytics providing the results of LIBS measurements on a meaningful sampling of natural (both cut and raw specimens) and synthetic rubies and sapphires, highlighting the potential of the method in helping gemological laboratories for the fast, easy, micro-destructive and reliable discrimination between natural and synthetic corundum, as well as provenance determination.*

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[2] G. Agrosi, G. Tempesta, E. Scandale, S. Legnaioli, G. Lorenzetti, S. Pagnotta, V. Palleschi, A. Mangone c, M. Lezzerini *Application of Laser Induced Breakdown Spectroscopy to the identification of emeralds from different synthetic processes*, *Spectrochimica Acta Part B*, 102, 2014, 48–51.

[3] M.S. Krzemnicki, H.A. Hänni, R.A. Walters, *A new method for detecting Be diffusion-treated sapphires: Laser-induced breakdown spectroscopy (LIBS)*, *Gems & Gemology*, 40, 2004, 314–322.

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## Handheld LIBS as a Field Tool for Diamond Exploration Analysis of Kimberlite Minerals.

Russell S. Harmon<sup>A</sup>, Richard R. Hark<sup>B</sup>, Chandra S. Throckmorton<sup>C</sup>, John J. Gurney<sup>D</sup>, Anthony H. Downey<sup>B</sup>, Andrew M. Somers<sup>E</sup>, and Leslie M. Collins<sup>C</sup>

<sup>A</sup>Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC 27695, USA

<sup>B</sup>Department of Chemistry, Juniata College, Huntingdon, PA 16652, USA

<sup>C</sup>Department of Electrical and Computer Engineering, Duke University, Durham, NC 27708, USA

<sup>D</sup>MS Group, 42 Morningside Road, N'dabeni, Cape Town 7405, South Africa

<sup>E</sup>SciAps, Inc., 2 Constitution Way, Woburn, MA 01801, USA

\*rsharmon@ncsu.edu

**ABSTRACT:** Garnet is commonly used as a geochemical pathfinder mineral in diamond exploration. Pyrope, the Mg-Al variety of garnet ( $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ), which is exceptionally rare in upper crustal rocks but transported to the Earth's surface in kimberlites and alkaline volcanic rocks produced in deep mantle sources, is the main garnet type of interest in this context. Kimberlite garnets associated with diamonds tend to be low-Ca, and Ti-poor, but enriched in Mg and Cr. The pyroxene diopside ( $\text{MgCaSi}_2\text{O}_6$ ) and the oxide minerals ilmenite ( $\text{FeTiO}_3$ ) and chromite ( $\text{FeCr}_2\text{O}_4$ ), are similarly useful in identifying diamondiferous kimberlites. A 2-part study was undertaken using the SciAps Z500 LIBS analyser to assess the potential for the in-field analysis of kimberlite minerals by handheld LIBS to distinguish between diamond-bearing and barren kimberlites. The first part of the study documented that the common garnet compositions can be readily discerned on the basis of their broadband LIBS spectra and the second part demonstrated that pyrope from kimberlites could be distinguished and diamond-bearing kimberlites recognized. Overall success for garnet type discrimination was 90.2%. Mn-Al spessartine, Ca-Cr uvarovite, and Fe-Al almandine were distinguished from the other Ca-Fe andradites, Ca-Al grossular garnet classes at success rates of 96-98%. Significant misclassification was observed only for the Fe-Al almandine, Ca-Fe andradites and Ca-Al grossulars, which form a complete solid solution series and which commonly occur in intermediate compositions. Pyrope from South Africa was discriminated from all other pyropes at ~90% success based on differences in the intensity of emission lines for Na, Mg, Ca, Al, Mn, Fe, Cr and Li. Likewise, different diamond-bearing kimberlites from within South Africa could likewise be confidently differentiated at an overall success of >96% with the loading weights for the same eight elements being associated with the discrimination. Suites of garnet + clinopyroxene  $\pm$  ilmenite  $\pm$  chromite were successfully utilized to discriminate 10 diamondiferous and 5 barren kimberlites from South Africa, Namibia, Canada, and the USA at 90% success, with emission lines for Mg, Ca, Cr, Ti, and Fe the most important contributors to the discrimination. These results highlight the potential that handheld LIBS, with its capability for the rapid chemical analysis in the field without the need for sample preparation, has to be an effective tool for mineral analysis and provenance determination in diamond exploration.

# *Geological Applications Session*

## ***Geo III***

*(Thu. 15<sup>th</sup> of June, h. 9.15-10.45)*



## **New Horizons in LIBS and Challenges for its Implementation in the Mining Industry**

M. Sabsabi\*, P. Bouchard, A. Harhira, J. El Haddad, K. Rifai, F. Vanier, A. Moreau, A. Blouin.

National Research Council Canada (NRC), Boucherville (QC), J4B 6Y4, Canada

\*mohamad.sabsabi@cnrc-nrc.gc.ca

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*ABSTRACT: The Laser-Induced Breakdown Spectroscopy (LIBS) technique has the advantage of analyzing the material without contact, thus making it suitable for in-the-field and real-time analysis of any type of materials, solid, liquid, slurries or gas. Because of its unique features, LIBS is currently a subject of great interest by several industrial sectors where there is a need for fast elemental analysis that cannot be addressed by conventional analytical methods. The driving force for this growth appears to be the unveiling of significant technological developments in the components (lasers, spectrometers, detectors) used in LIBS instruments, as well as emerging needs to perform real time measurements under conditions to which conventional techniques cannot be applied.*

*The LIBS principle of operation is quite simple, although the physical processes involved in the laser-matter interaction are complex and still not completely understood. In this presentation, we will highlight lessons learned from experience in the implementation of the LIBS technique, the pros and cons on what to do and avoid. In addition we will outline NRC activities in the development of LIBS technique and its applications for on-line measurements in various fields in the mining sector. Based on these applications, we will discuss the LIBS instrumentation in terms of robustness, analytical performance for the mining value chain and comparison to conventional techniques. We will also present a case study with focus on LIBS for gold detection in ore samples for the mining industry.*

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## Investigation of Normalization Methods using Plasma Parameters for Laser Induced Breakdown Spectroscopy (LIBS) under simulated Martian Conditions

Kristin Rammelkamp<sup>\*A</sup>, David S. Vogt<sup>A</sup>, Susanne Schröder<sup>A,B</sup>, Heinz-Wilhelm Hübers<sup>A,C</sup>

<sup>A</sup>Institute of Optical Sensor Systems, German Aerospace Center (DLR), 12489 Berlin, Germany;

<sup>B</sup>Institut de Recherche en Astrophysique et Planétologie (IRAP), Toulouse, France;

<sup>C</sup>Department of Physics, Humboldt Universität zu Berlin, 12489 Berlin, Germany.

\*kristin.rammelkamp@dlr.de

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**ABSTRACT:** The LIBS technique has become an important method for the elemental analysis of rocks and soils on Mars [1]. The ChemCam instrument, that is part of the NASA mission Mars Science Laboratory applies LIBS at stand-off distances since 2012 ([2],[3]). Due to its achievements the follow up instrument SuperCam of the Mars 2020 mission will also use LIBS in combination with other spectroscopic methods [4]. Since LIBS measurements are influenced by matrix effects and varying experimental conditions the data needs to be normalized. This is especially important for LIBS applications in the field of planetary exploration, as the encountered geological samples show variations on different scales and the measurement parameters are not fixed like in a laboratory. Several normalization methods have been proposed in previous studies, such as using the total emission intensity [5], the emission intensity with continuous emission removed [6], the C(I) 247 nm peak [7] or the plasmas continuous emission [8]. It was shown that these approaches can work well under specific conditions, but do not provide a general normalization method. In this study we test an approach that uses plasma parameters, namely temperature and electron density, for the normalization under Martian conditions. In the work of [9] and [10] this method was applied to terrestrial laboratory LIBS data of glass and steel samples. Both observed reduced fluctuations in shot-to-shot measurements.

The LIBS set-up at DLR has an Echelle spectrometer (UV: 190-375 nm and NIR: 270-850 nm, Aryelle Butterfly, LTB), a simulation chamber, where pressure and atmospheric composition can be adjusted, a 1064 nm Nd:YAG laser (10 Hz repetition rate, 8 ns pulse length) and a time-gated intensified CCD camera. We investigated various geological samples relevant for Mars such as basalts and andesites to test which normalization is best suited for LIBS data taken under Martian atmospheric conditions. The influence on univariate and multivariate calibration will be analyzed. Moreover, we are testing combinations of different normalization methods and compare the results to the commonly applied methods. Advantages and drawbacks for different sample types will be discussed.

**References:** [1] Maurice et al. (2016), *J. Anal. At. Spectrom.*; [2] Wiens et al. (2012), *Space Sci. Rev.*; [3] Maurice et al. (2012), *Space Sci. Rev.*; [4] Clegg et al. (2015), <sup>46th</sup> LPSC, #2781; [5] Body and Chadwick (2001), *Spectrochim. Acta B*; [6] Wiens et al. (2013), *Spectrochim. Acta B*; [7] Rapin et al. (2016), *Earth and Planetary Sc. Letters*; [8] Schröder et al. (2015), *Icarus*; [9] Panne et al. (1998), *Spectrochim. Acta B*; [10] Feng et al. (2010), *Spectrochim. Acta B*

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## Mapping the geochemical stratigraphy of Mt. Sharp in Gale Crater, Mars, using the ChemCam instrument on the NASA Curiosity rover

Jens Frydenvang<sup>\*A</sup>, Olivier Forni<sup>B</sup>, Agnes Cousin<sup>B</sup>, Roger C. Wiens<sup>C</sup>, Nicolas Mangold<sup>D</sup>, Olivier Gasnault<sup>B</sup>, Sylvestre Maurice<sup>B</sup> and the ChemCam Team

<sup>A</sup>Natural History Museum of Denmark, University of Copenhagen, Copenhagen, Denmark;

<sup>B</sup>Institut de Recherche en Astrophysique et Planétologie, University of Toulouse, CNRS, Toulouse, France.

<sup>C</sup>Los Alamos National Laboratory, ISR-2, Los Alamos, USA

<sup>D</sup>Laboratoire de Planétologie et Géophysique de Nantes, Université de Nantes, Nantes, France

\*jrydenvang@snm.ku.dk

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*ABSTRACT: The ChemCam instrument on board the NASA Mars Science Laboratory (MSL) Curiosity rover is the first Laser-Induced Breakdown Spectroscopy instrument operating on another planet. The main scientific goal of the MSL mission, is to investigate the layers of Mt. Sharp (formally Aeolis Mons), a 5-km high sedimentary mound in the center of Gale Crater, Mars, for clues to the past habitability of Mars. These sedimentary layers of Mt. Sharp provide a geological record of the transition between the ancient wet climate on Mars, featuring long-lived lakes on the surface, towards the hyper-arid climate observed on Mars today. Due to the low cost of LIBS measurements in terms of both time and power, ChemCam is active on most sols (Mars solar days), and thus uniquely capable of tracking fine-scale bedrock chemistry variations observed as the Curiosity rover continues to climb up Mt. Sharp. This enables us to recreate the geochemical stratigraphy of Mt. Sharp in unparalleled spatial resolution. The up-to-date geochemical stratigraphy of Mt. Sharp will be presented, and the issues related to using LIBS for planetary rover missions – including comparisons to other chemistry instruments on the Curiosity rover - will be discussed.*

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## Iodine determination by high resolution continuum source molecular absorption spectrometry: A comparative between promising molecules.

Mauana Schneider<sup>A</sup>, Mao-Dong Huang<sup>B</sup>, Helmut Becker-Ross<sup>B</sup>, Bernhard Welz<sup>A,C</sup>

<sup>A</sup>Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis, Brazil; <sup>B</sup>ISAS – Leibnitz Institute for Analytical Sciences, Berlin, Germany, <sup>C</sup>Instituto Nacional de Ciência e Tecnologia do CNPq, INCT de Energia e Ambiente, Universidade Federal da Bahia, Salvador, BA, Brazil.

mauana.schneider@gmail.com

*Abstract: The direct determination of halogens by conventional atomic absorption spectrometry is not possible, once their resonance lines are below 190 nm in the vacuum-UV. An alternative for the atomic resonance lines is the indirect determination via diatomic molecules composed by the halogen and a molecule-forming reagent. The gaseous diatomic molecules are able to absorb radiation in the ultraviolet and visible wavelength range and like the absorbance of atoms, that of diatomic molecules also obeys Lambert-Beer's law. In the 1980s and 1990s some workers proposed the use of line-source atomic absorption spectrometers for the determination of halogens, using wavelengths, emitted by a line source that accidentally coincided with a molecular absorption band; however this practice was susceptible to interferences since the spectral neighborhood was unknown and the available background correction systems failed. Thus, the low-resolution monochromator of line-source atomic absorption spectrometers cannot separate correctly the fine structure of the molecular bands. With the advent of high-resolution continuum source atomic absorption spectrometry, the determination of halogens via diatomic molecular spectra became possible due to the high-resolution monochromator system), providing a better split of the wavelengths, a high intensity xenon arc lamp emitting a continuum between 190 nm and 890 nm, and a CCD array detector, which permits a three-dimensional view of the spectra and the spectral neighborhood. These features made the determination of halogens possible with low limits of detection when compared with electrochemical or classic methods. Several papers have been published describing the determination of fluorine, chlorine and bromine, using a series of metals as reagents, which are able to form a diatomic molecule with the halogen at high temperatures provided by the electrothermal vaporization. However, there is a lack of publications about iodine determination by HR-CS GF-MAS; the reason is the low dissociation energy of the diatomic molecules formed with iodine, less than 500 kJ mol<sup>-1</sup>, which turns the molecule unstable at high temperatures and, in the presence of other halogens, the competition for the molecule-forming reagents results in low sensitivity and interferences. Some diatomic molecules of iodine presented a good thermal stability, even with dissociation energy lower than 500 kJ mol<sup>-1</sup>, when submitted to an optimized temperature program, such as BaI, which exhibits high sensitivity when pyrolysis temperatures up to 600 °C and a vaporization temperature of 2000 °C were applied in a graphite tube without permanent modifier [1]. Calcium can also be used as molecule-forming agent and, with an optimized temperature program of 1500 °C pyrolysis and 2500 °C vaporization temperature, using an iridium-coated tube, produces a highly sensitive band. This work presents a comparison between CaI, BaI, SrI and YI molecules, studying their characteristic mass, thermal stability, permanent modifiers, possible interferences, more sensitive wavelengths and possibilities of applications. [1] M.D. Huang, H. Becker-Ross, S. Florek, M. Okrus, B. Welz, S. Morés, Spectrochim. Acta Part B 64 (2009) 697.*

## Characterization of NWA 6286 and NWA 7857 Ordinary Chondrites Using X-Ray Diffraction, Magnetization Measurements and Mössbauer Spectroscopy

A.A. Maksimova<sup>A</sup>, M.I. Oshtrakh<sup>\*,A</sup>, A.V. Chukin<sup>A</sup>, I. Felner<sup>B</sup>, G.A. Yakovlev<sup>A</sup>, V.A. Semionkin<sup>A</sup>

<sup>A</sup>Institute of Physics and Technology, Ural Federal University, Ekaterinburg, 620002,  
Russian Federation;

<sup>B</sup>Racah Institute of Physics, The Hebrew University, Jerusalem, Israel

\*oshtrakh@gmail.com

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*ABSTRACT: Two fragments of ordinary chondrites NWA 6286 LL6 and NWA 7857 LL6 were characterized using optical and scanning electron microscopy with energy dispersive spectroscopy, X-ray diffraction, magnetization measurements and Mössbauer spectroscopy. We observed in these meteorites: i) some variations in the phase composition, ii) small variations in Mössbauer hyperfine parameters for some identical phases, and iii) difference in the saturation magnetic moment. The distribution of  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  between the M1 and M2 sites in the silicates and the temperatures of cations distribution equilibrium in olivine and orthopyroxene were estimated by using X-ray diffraction and Mössbauer spectroscopy.*

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# *Coal and Steel Analysis Session*

*(Tue. 13<sup>th</sup> of June, h. 11.15-13.15)*

## A set of quantification method for coal analysis using laser-induced breakdown spectroscopy

Zhe Wang\*, Zongyu Hou, Zheng Li, Weidou Ni, Hualiang Yin, Yangting Fu, Tianqi Li

Department of Thermal Engineering, Tsinghua-BP Clean Energy Center, Tsinghua University, Beijing, China

\*zhewang@tsinghua.edu.cn

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**ABSTRACT:** Laser-induced breakdown spectroscopy (LIBS) has shown great potential in coal analysis, steel analysis, environmental monitoring, etc. However, low sample-to-sample reproducibility of LIBS is the most critical obstacle for accurate quantification and wild commercialization of the technology. Averaging multi-pulse normalized spectra was nearly the only applied method to improve the sample-to-sample reproducibility, while the method can only improve the reproducibility to some extent. In addition, the measurement accuracy of LIBS was also limited due to matrix effects. In this work, the resource for generating measurement uncertainty was analyzed and method was proposed to improve the measurement reproducibility. A set of method to improve both precision (sample-to-sample reproducibility) and accuracy for LIBS quantification was then proposed. The method includes three steps: 1) the intensities of all spectral lines from every single pulse are converted to a standard state value using a “spectrum standardization” method to reduce the measurement uncertainties to some acceptable levels; 2) the standardized spectra are compared with a large spectral database for identification to check whether the current measured sample is a new sample or has already been in the database with known composition/property information; 3) if the sample is found to be a new sample, a dominant factor based partial least square (PLS) model will be applied to provide quantitative analytical results and the new standardized spectral information and analytic results are inserted into the spectrum database, making the database self-adaptable for future measurement; while if the sample is found to be already in the database, the analytic result will be directly obtained from the database. The proposed method was applied for coal analysis. Results showed that the relative standard deviations (RSD) of carbon for different measurements of the same sample become 0.3%, proving that LIBS is able to providing high reproducibility at least for coal analysis applications. The average measurement errors for carbon, hydrogen, volatile, ash, heat values is 0.42%, 0.05%, 0.07%, 0.17% and 0.07MJ/kg, respectively, and all of these measurement accuracies have totally reached the requirement by the national standard of China for coal analyses using traditional chemical methods. This is the first qualified quantitative application for LIBS with real industrial requirement and the present work proved the feasibility of LIBS for accurate quantification from technical point of view.

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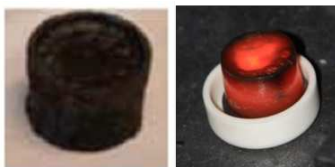
## Analysis of metallurgical slags in steel production by calibration-free laser – induced breakdown spectroscopy

Simon Eschlböck-Fuchs <sup>A, B</sup>, Roman Rössler <sup>B</sup>, Christoph M. Ahamer <sup>A</sup>, Ludwig Birklbauer <sup>A</sup>, Norbert Huber <sup>A</sup>, Johannes D. Pedarnig <sup>\*A</sup>

<sup>A</sup> Institute of Applied Physics, Johannes Kepler University, Altenberger Straße 69, 4040 Linz, Austria  
<sup>B</sup> voestalpine Stahl GmbH, A-4031 Linz, Austria

\* johannes.pedarnig@jku.at

**ABSTRACT:** More than 230 slag samples from secondary metallurgy are taken during steel production and analyzed at-line by laser-induced breakdown spectroscopy (LIBS). The slags consist of several major and minor oxides (CaO, Al<sub>2</sub>O<sub>3</sub>, MgO, SiO<sub>2</sub>, FeO, MnO, TiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, ...) with varying concentrations. Plasma is induced by single-pulse Nd:YAG laser radiation (1064 nm) and the plasma radiation is detected in collinear geometry with Echelle spectrometer and time-gated ICCD camera [1]. Off-line reference analysis of the oxide concentrations  $C_N$  in slags are performed by X-ray fluorescence spectrometry (XRF). An automated calibration-free (CF) LIBS system is employed to measure spectra in the UV and VIS ranges and to quantify the concentration  $C_{CF}$  of the major oxides. The total time-to-analysis from slag sampling to CF-LIBS calculated oxide concentrations is around 3 minutes per sample. The major oxide concentrations determined by CF-LIBS and XRF are compared. The stability of analysis, the influence of sample homogeneity/heterogeneity and temperature, and the errors of concentration are investigated. The minor oxide P<sub>2</sub>O<sub>5</sub> is analyzed by calibration-based LIBS using XRF data as reference. The influence of gas purge and of matrix normalization on the limits of detection is investigated. The errors of CF-LIBS and calibration-based analyses are compared for slags from the production and for homogenized slags.



Photos: voestalpine Stahl GmbH

[1] C.M. Ahamer et al., Laser-induced breakdown spectroscopy of major and minor oxides in steel slags: Influence of detection geometry and signal normalization, *Spectrochimica Acta Part B* 122 (2016) 157-164.

*Acknowledgements:* Financial support by the Austrian Research Promotion Agency FFG (Project 838861) is gratefully acknowledged.

## Strategies for the LIBS on-line analysis of transition billets in continuous casting machines

Guy Monfort<sup>\*A</sup>, Geneviève Moréas<sup>B</sup>

<sup>A</sup>Industrial Solutions Unit, CRM Group, Liège, Belgium;

<sup>B</sup>Department Industrial Process Control and Measurements, CRM Group, Liège, Belgium.

\*guy.monfort@crmgroup.be

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**ABSTRACT:** *In the continuous casting of stainless steels and tool steels, several material grades are sequentially produced on the same machine. Changing from one composition to the other is done without stopping and restarting the continuous caster, mainly for productivity reasons. As a result, a certain length of the cast material has a composition intermediate between the one of the first and of the second grade. This so-called transition billet must be cut away and cannot be sold as such: it is usually recycled in the process. For economic reasons, the length of this transition billet has to be kept to a minimum but, in the absence of an on-line chemical analysis, some extra-length has to be accounted for as a safety margin. Hence, in order to save material, it would be of the highest interest to be able to assess on-line the exact position where the final required steel composition is reached.*

*In the scope of the European project LACOMORE, laboratory and industrial tests were carried out in order to determine the position of the transition by on-line LIBS measurements. One of the main difficulties in this application of the LIBS technique is the presence of a rather thick oxide layer at the surface of the billet, the composition of which can differ from the bulk due to the preferential migration of some elements into the oxide. Several techniques were applied by the researchers involved in the project to minimize the impact of the oxide layer on the determination of the transition (Metallurgical model, Artificial Neural Networks, discriminant functions, sophisticated statistical analysis...). Several publications on these topics by the corresponding authors are now available in the literature.*

*In this paper, two complementary approaches are evaluated for the minimization of the impact of the oxide layer. The first method consists in increasing the number of measurements to get an accurate statistical representativeness of the oxide composition. The setup used is described and the evaluation of the obtained precision on the position of the transition is given. The implications on the industrial implementation are also discussed. The second approach aims at measuring the bulk composition of the material by penetrating through the oxide layer while the billet is moving. Two procedures have been tested to reach this goal: the first one uses a very high repetition rate laser (up to 100 kHz) which is fast enough to generate several pulses at the same place despite the billet movement. This paper describes the practical implementation of the method, and evaluates its efficiency through the examination of the depth of the laser impacts by several techniques. The advantages and drawbacks of this kind of lasers for the addressed purpose are also commented. Finally, the paper analyses the possibility of applying a beam steering technique to aim several pulses of a 20 Hz laser at the same place, digging through the oxide. The method is based on an image analysis algorithm controlling a beam steering device in closed loop.*

*Finally, the industrial applicability and the advantages and limitations of these techniques are discussed in the scope of the analysis of transition billets but also for other industrial applications.*

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## Dynamics and Parameters of Plasma Generated by Long and Short Dual Pulses Laser Interacting with Steel Sample

M.C. Cui<sup>A,B</sup>, Y. Deguchi<sup>B\*</sup>, Z.Z. Wang<sup>B,C</sup>, Y. Fujita<sup>B</sup>, R.W. Liu<sup>B</sup>

<sup>A</sup>School of Mechanical Engineering, Xi'an Jiaotong University, Xi'an, China;

<sup>B</sup>Graduate School of Advanced Technology and Science, Tokushima University, Tokushima, Japan

<sup>C</sup>State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an, China.

\*ydeguchi@tokushima-u.ac.jp

**ABSTRACT:** Laser-Induced Breakdown Spectroscopy (LIBS) as a promising elemental analytical method has been widely studied for iron-making process [1]. With the features of fast response, real-time and non-contact, LIBS can be applied to the iron-making plants. It is vital for analytical precision of LIBS to generate a uniform and stable plasma. In previous study, the long-short dual-pulse LIBS (DP-LIBS) were employed to measure the metallic samples [2]. A long pulse-width laser beam was used to control the plasma cooling process during the LIBS measurement. In order to study the long-short dual pulse LIBS in detail, the dynamics and parameters of the plasma, which is generated by long and short dual pulses laser, are investigated through observation of plasma emission and calculation of plasma parameters in this study.

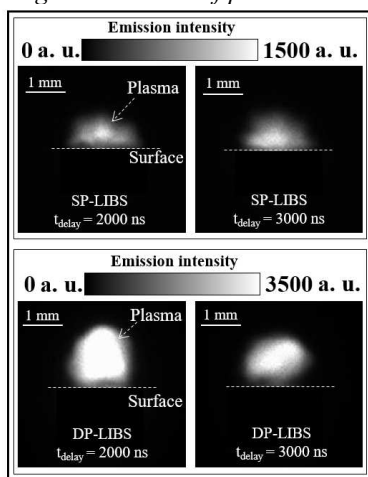


Fig.1 Images of the plasma dynamics

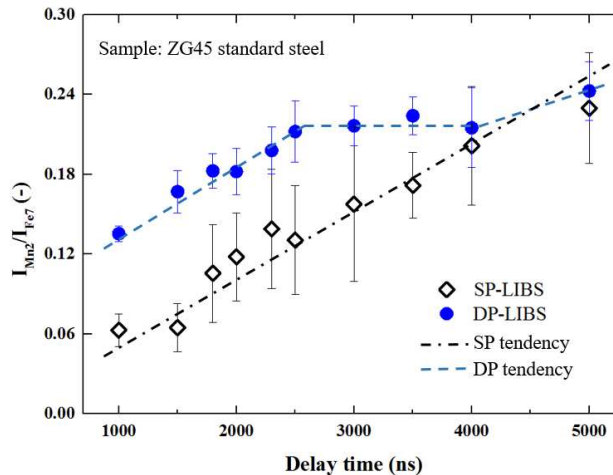


Fig.2 Intensity ratio of Mn/Fe

Fig.1 shows the images of the plasma dynamics using SP-LIBS (single-pulse LIBS) and DP-LIBS. The plasma is stronger and more uniform when using the long-short dual pulses laser. The delay time dependence of intensity ratio of manganese line and iron line is shown in Fig.2. Using SP-LIBS, the intensity ratio of Mn/Fe continuously increases as the delay time increasing. Compared with SP-LIBS, the increase of the intensity ratio becomes slow using the long and short DP-LIBS. It is worthy to notice that the intensity ratio seems to be constant around delay time 3000 ns. The plasma observation and ratio calculation results demonstrate that the long-short dual pulses laser can generate a more stable and uniform plasma from the steel sample. Thus the long and short dual pulses laser is a promising way to produce signals for LIBS measurement.

[1] Y. Deguchi, *Industrial Applications of Laser Diagnostics* (CRC Press, New York, 2011), 107-133.

[2] Z. Wang, Y. Deguchi, et al. "Emission characteristics from laser-induced plasma using collinear long and short dual-pulse LIBS". *Appl. Spectrosc.* 2017. accepted.

## Fast Identification of Steel Bloom Composition at a Rolling Mill by LIBS Elemental Analysis

Volker Sturm<sup>\*A</sup>, Christoph Meinhardt<sup>B</sup>, Rüdiger Fleige<sup>A</sup>, Cord Fricke-Begemann<sup>A</sup>, Jens Eisbach<sup>C</sup>

<sup>A</sup>Fraunhofer-Institut für Lasertechnik ILT, 52074 Aachen, Germany;

<sup>B</sup>RWTH Aachen University, Lehrstuhl für Lasertechnik, 52074 Aachen, Germany;

<sup>C</sup>Deutsche Edelstahlwerke Specialty Steel GmbH & Co. KG, 57078 Siegen, Germany.

\*volker.sturm@ilt.fraunhofer.de

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*ABSTRACT: Laser-induced breakdown spectroscopy (LIBS) is applied for the elemental analysis of steel blooms in a rolling mill. The 2-3 tons steel blooms with superficial scale are transported in a sequence on a roller table to successive processing steps. Laser ablation of the scale and the analysis of the subsurface bulk steel is carried out using the same laser in less than 50 s during scheduled stop times of the roller table. Up to 14 elements are measured for several hundreds of blooms of low and high alloy steel during routine production. The results are compared with the nominal compositions of the rolling sequence which demonstrates the feasibility for material identification.*

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## Recent Developments in Handheld LIBS and New Applications in Steel Analysis

David R. Day\*, Brendan Connors, and Jeroen van Run

2 Constitution Way, Woburn, MA, 01801, USA

\*dday@sciaps.com

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*ABSTRACT: SciAps recently introduced its second-generation handheld LIBS analyzer with several enhancements which include size and weight reduction, wider spectral range, higher laser shot rate, among others. In this presentation, we will first review the technical capabilities and recent improvements. These improvements have opened the door for more accurate steel analysis including testing for carbon and silicon in low alloy and carbon steels. Quantifying carbon content, particularly in the range of 0 – 1%, is crucial for grade separation and assessing physical properties of carbon steels. Monitoring of low silicon content in carbon steels is useful for industrial applications, particularly petrochemical refining where silicon can protect against corrosion in high temperature processes. We will present data from both lab and in-service steels showing reliable quantification of carbon as low as 0.1% and silicon as low as 0.02%.*

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## Trace-metal Mobility in Coal Samples using Multivariate Optimised Microwave Based Sequential Extraction Method prior to Spectrometric Determination

Nomvano Mketo<sup>AB\*</sup>, Philiswa N. Nomngongo<sup>B</sup>, J. Catherine Ngila<sup>B</sup>

<sup>A</sup>Analytical Facility, University of Johannesburg, P.O. Box: 524, Auckland Park 2006, South Africa;

<sup>B</sup>Department of Applied Chemistry, University of Johannesburg, PO Box 17011, Doornfontein 2028, Johannesburg, South Africa.

[\\*nomvano.mketo@gmail.com](mailto:nomvano.mketo@gmail.com) or nmketo@uj.ac.za

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**ABSTRACT:** Trace-metals form part of coal contaminants and they occur in different modes. The difference in bonding for these elements depends on their chemical properties. Therefore, the mobility behavior of trace-metals must be evaluated to get more insight on their eco-toxicity. Hence, this work describes the development of a rapid microwave-assisted sequential extraction (MW-ASE) method followed by ICP-MS analysis for determination of metal mobility in coal samples. Five different extraction reagents [Milli-Q water, HCl (5M), HNO<sub>3</sub> (2M), H<sub>2</sub>O<sub>2</sub> (3M) and HNO<sub>3</sub> (7M)] were utilised and key parameters such as temperature, time, and sample amount were optimized using multivariate approach. Under optimum conditions, V, Ga, Sr and Ba were the only metals that showed solubility towards water, therefore, they can be classified as highly mobile and eco-toxic under wet conditions. Additionally, all the investigated metals showed solubility towards acidic conditions (HCl & HNO<sub>3</sub>). These results, suggest that, the metals are predominantly bonded to the sulphate, sulphide, and carbonate minerals of the coal. Under oxidized environment (H<sub>2</sub>O<sub>2</sub>), most metals showed some solubility except for Sr, Ce and Pb. Strontium and lead were 100 % extracted from coal using the previous reagents, but Ce showed total extraction recovery of 90 % only while Y was only recovered at 80 %. Therefore, these two metals have strong affinity towards clay and silicon minerals, hence, they can only be 100 % released from coal when notorious HF is used as one of the extracting reagents.

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## *LIBS Imaging Session*

*(Tue. 13<sup>th</sup> of June, h. 11.15-13.15)*



## Elemental imaging by LIBS: recent advances and remaining challenges

V. Motto-Ros<sup>\*A</sup>, F. Pelascini<sup>B</sup>

<sup>A</sup>Institut Lumière Matière, UMR5306 Université Lyon 1-CNRS, 69622 Villeurbanne, France

<sup>B</sup>CRITT Matériaux Alsace, 67305 Schiltigheim, France

\* [vincent.motto-ros@univ-lyon1.fr](mailto:vincent.motto-ros@univ-lyon1.fr)

**ABSTRACT:** The imaging capability of laser-induced breakdown spectroscopy (LIBS) has a high potential in various domains including biology, industry, geology and medicine (figure 1). This approach can be distinguished by its ease in use, multi-elemental capability, detection of light elements, as well as operation at ambient conditions. This is furthermore the only all-optical technique providing space-resolved elemental information with ppm-scale sensitivity and  $\mu\text{m}$ -range resolution. These advantages, make LIBS imaging very attractive to be used in research laboratories for routine investigations.

However, advanced technological solutions must be found for this application since elemental imaging requires high sensitivity, sharp spatial resolution, high speed of acquisition as well as the ability to process a huge quantity of data. In this presentation, we will summarize the recent progresses made in the Light and Matter Institute and the CRITT concerning the implementation of the LIBS imaging. Different examples will be shown with the aim of illustrating the specificities of LIBS among other elemental imaging approaches, such as the possibility to detect and image light elements, the coupling with optical and Raman imaging and the analysis of large-scale samples. Different perspectives and remaining challenges will be finally proposed.

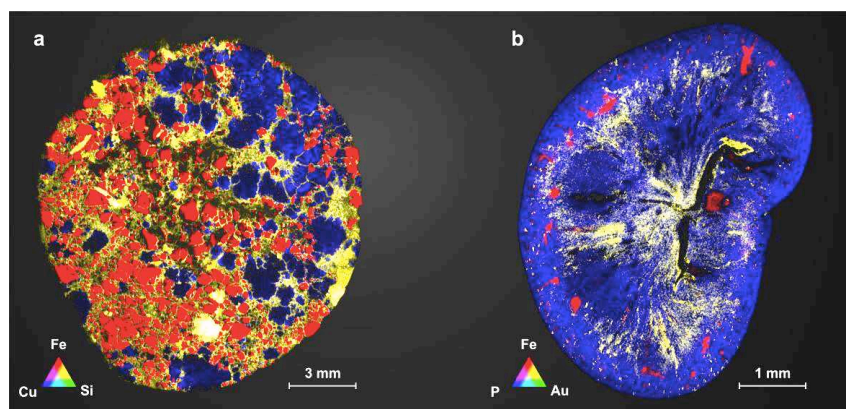


Figure 1: Examples of elemental images represented in false color scale, a) megapixel images of a turquoise gem stone, b) Mouse kidney 1h after gold nanoparticles administration.

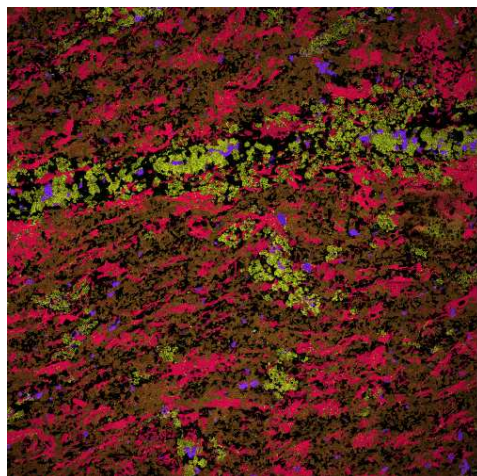
## LIBS Imaging of Drill Core Samples for the Mining Exploration

François R. Doucet<sup>\*A</sup>, Lütü-Çelebi Özcan<sup>A</sup>, Dominique Doucet<sup>B</sup>

<sup>A</sup>ELEMISSION Inc., 108-4030, Côte-Vertu, Montréal, QC, CANADA, H4R 1V4; <sup>B</sup>Sirios Resources Inc., 1000 Rue Saint-Antoine O, Montréal, QC, CANADA, H3C 3R7;

\*fdoucet@elemission.ca

**ABSTRACT:** Detailed geological models and mineralogy knowledge greatly assist the mining industry in locating mineral resources, and can reduce the need for expensive drilling, saving time and money. LIBS logging technology provides a highly selective and sensitive means of gaining this information from materials and drill cores derived from drilling. Until recently, geologists, metallurgists, and geotechnical engineers had to manually interpret and record minerals found in these materials.



25 x 25 mm<sup>2</sup> scan of a core sample with 50µm spatial resolution that represent 251 001 LIBS spectra acquired in 4 minutes.

This manual method – the visual interpretation of drill cores – is labor intensive and subject to human error. LIBS technology enables a systematic and selective way – based on the physics of atomic emission spectroscopy (AES) – to minimize or eliminate human error via automation. Small gold nuggets, which cannot be seen by the human eye (i.e. less than 150 µm), are revealed by LIBS imaging. An intelligent, automated instrument that can flag gold nuggets and map different geochemical deposits in drill cores has been developed for the mining industry. When benchmarking this drill core analyzer against existing technology, it is possible to see the significant advantage that can be achieved with this technology in the mining industry. First, LIBS imaging provides the highest selectivity for elemental imaging through atomic emission spectroscopy. Second, the surgical resolution of laser ablation, the ease of scanning a large area and adapting to any sample shape and size, makes the instrument the best solution for permanent core logging. Hence, logged data can be used to discover new exploitable mines in the future using data mining, when other element demand becomes economically viable to extract. LIBS logging technology has the potential to eliminate the need for keeping drill core samples in core shacks as prescribed by the authorities. The results obtained using this drill core analyzer enable the logging of 200 to 1000 meters of drill core samples per day. The results presented in this paper demonstrate that miniscule gold nuggets can be easily outlined on drill core samples coming from different types of mineralogical assemblages (e.g. pyrite, marcasite, arsenopyrite). In addition, the results show that different typical geochemical signatures can be identified using an intelligent algorithm. The high throughput analysis demonstrated here showcases LIBS logging technology as a potential game changer in the field of mining exploration.

## Influence of grain sizes on the quantification of LIBS measurements in concrete

Cassian Gottlieb\*, Tobias Günther, Steven Millar, Nina Sankat, Gerd Wilsch

Bundesanstalt für Materialforschung und –prüfung (BAM), Unter den Eichen 87, 12205 Berlin, Germany

\*cassian.gottlieb@bam.de

**ABSTRACT:** Concrete is a multiphase material made of cement, aggregates and water. The heterogeneity of concrete is a result of mixing aggregates (grain size between 0.125 mm to 32 mm) and cement (grain size < 0.04 mm) together. There are always aggregates with a grain size below 0.125 mm (flour grains) therefore the cement matrix is always a mixture of these small particles. Different grain size distributions by making concrete are important to ensure the needed density and compressive strength. In order to estimate the remaining lifetime of concrete structures the quantification of element concentrations of alkali and chlorides regarding to the cement matrix only (1/3 of the total mass), is a major concern in civil engineering [1]. Due to two-dimensional scanning with LIBS the coarse aggregates can be evaluated and excluded from the analysis (see figure 1, left). In the case of particles (flour grains and cement) smaller than the laser spot size, the microscopic heterogeneity influences the laser-plasma interaction and has therefore an impact on the results (see figure 1, right). In this study the influence of the micro-heterogeneity and the impact on the laser-material interaction is examined [2-3]. The effect of changing ratios between cement particles and aggregate particles in the laser-induced plasma has been analyzed (see figure 1, right). Therefore, different samples with defined grain sizes are prepared and the obtained distributions were analyzed with x-ray diffraction (XRD). For the LIBS measurements, an automated system that operates with a low energy NdCr:YAG laser (pulse energy of 3 mJ, a wavelength of 1064 nm, a pulse width of 1.5 ns, a repetition rate of 100 Hz) and a NIR Czerny-Turner spectrometer has been used.

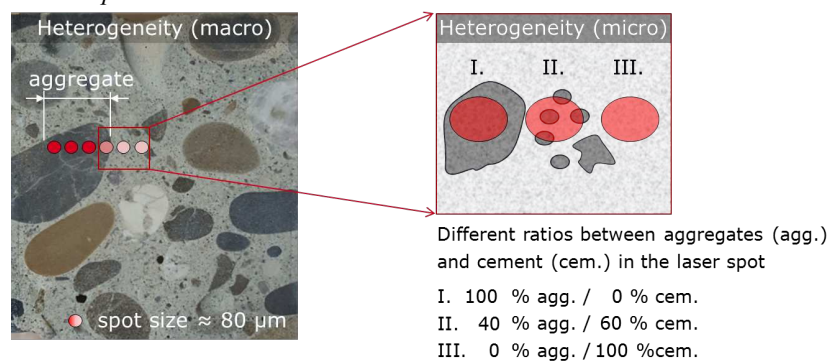


Figure 1: Photo of a concrete sample with visible coarse aggregates (left). Illustration of the micro-heterogeneity. The distribution of different grains may have a great impact on the evaluation (right).

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## **Integrated Laser Sensor (ILS) for characterization and extended mapping of remote targets**

Violeta Lazic, Antonio Palucci, Marcello Nuvoli, Marco Pistilli, Ivano Menicucci, Francesco Colao, Luigi De Dominicis, Salvatore Almaviva

ENEA, Dep. FSN-TECFIS-DIM, Via E. Fermi 45, 00044 Frascati (Italy)

\*violeta.lazic@enea.it

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*ABSTRACT: Here we present an innovative Integrated Laser Sensor (ILS) that combines four different laser spectroscopic techniques and two vision systems in a unique, transportable instrument. The ILS is equipped with an autofocus and performs scanning over a target at distances between 8 and 50 meters with chosen grid density. The system is self-powered and remotely controlled via wireless communication, thus it could be employed also in hazardous areas. Beside the visual inspection with a low or a high magnification, a powerful combination of different spectroscopic techniques allows collecting information about: material change from one scanning point to another, presence of surface contaminants, surface's molecular composition and elemental composition of top target layers, the latter achieved by LIBS (Laser Induced breakdown Spectroscopy). ILS has been fully developed at ENEA for security applications under EU FP7 project EDEN, and it was successfully tested in two outdoor campaigns. However, ILS has a great potential in many other applications and has been already employed for characterization rocks materials and for Cultural Heritage.*

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## LIBS-Stratigraphy of protective coatings: Investigations on the wavelength dependence of the ablation rate in metals

Morris J.J. Weimerskirch<sup>\*A</sup>, Tristan O. Nagy<sup>B</sup>, Ariane Giesriegl<sup>C</sup>, Ulrich Pacher<sup>B</sup>, Wolfgang Kautek<sup>B</sup>

<sup>A</sup>Faculty of Physics, University of Vienna, Boltzmanngasse 5, 1090 Wien, Austria;

<sup>B</sup>Department of Physical Chemistry, University of Vienna, Währingerstrasse 42, 1090 Wien, Austria;

<sup>C</sup>Faculty of Physics, Technical University of Vienna, Wiedner Hauptstr. 8, 1040 Wien, Austria.

\*ix@nawi.at

**ABSTRACT:** LIBS-Stratigraphy<sup>[1,2]</sup> was applied to the investigation of galvanised steel sheets as a typical modern multi-layer coating system for environmental corrosion protection. The samples were ablated stepwise by the use of two different wavelengths of a frequency-converted Nd:YAG-laser, 266 nm and 532 nm, with a pulse duration of  $\tau = 4 - 10$  ns at fluences ranging from  $F = 50 - 250$  J/cm<sup>2</sup>.

The emission light of the resulting plasma was analysed as a function of both penetration depth and elemental spectrum in terms of linear correlation analysis<sup>[3]</sup>. Elemental depth profiles were calculated and compared to EDX-cross sections of the cut sample.

A mathematical algorithm designed for the reconstruction of layer structures from distorted emission traces, caused by the Gaussian ablation profile<sup>[2,4]</sup> can resolve even thin intermediate layers in terms of depth and thickness. The obtained results were compared to a purely thermally controlled ablation model.

Thereby deviations in the ablation behaviour of Al but not of Ni are witnessed. The average ablation rate ( $h$ ) as a function of fluence  $F$  for Ni ranges from  $1 - 3.5$   $\mu\text{m/pulse}$  for  $\lambda = 266$  nm as well as for  $\lambda = 532$  nm. In contrast, the  $h$  range for Al differs from  $2 - 4$   $\mu\text{m/pulse}$  for  $\lambda = 532$  nm and  $4 - 8$   $\mu\text{m/pulse}$  for  $\lambda = 266$  nm in the exact same fluence range on the exact same sample. This points towards an element-selective wavelength-dependent plasma coupling<sup>[5]</sup> which influences the metal ablation with pulsed ns-lasers in addition to thermal heat transfer in the bulk metal.

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## Advances in direct utilization of echellograms in LIBS analysis

Pavel Pořízka<sup>\*A,B</sup>, Jakub Klus<sup>A,B</sup>, David Prochazka<sup>A,B</sup>, Jakub Vrábel<sup>A</sup>, Jan Novotný<sup>A,B</sup>, Jozef Kaiser<sup>A,B</sup>

<sup>A</sup>CEITEC BUT, Central European Institute of Technology, Brno University of Technology, Purkyňova 123,  
61200 Brno, Czech Republic;

<sup>B</sup>AtomTrace, a.s., Kolejní 9, 61200 Brno, Czech Republic;

\*pavel.porizka@ceitec.vutbr.cz

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**ABSTRACT:** In our recent study we have proved beneficial utilization of echellograms in Laser-Induced Breakdown Spectroscopy (LIBS) experiment. sCMOS detectors provide the option to detect spectrally resolved information selectively, i.e. to readout only certain pixels from the whole image on the detector. This leads to significant decrease of readout time and thus to possibility of high repetition rate laser sampling (up to kHz).

In this work we aim to advance direct utilization of echellograms in LIBS experiment. Qualitative elemental analysis based on position in echellograms was provided, hence giving basic library of most common spectral lines. Performances of several algorithms for identification of peak positions were compared. Classification of steels and aluminum alloys certified reference materials was assessed employing linear and non-linear chemometric algorithms applied on typical 1D LIBS spectra as well as selection of echellograms pixels (spectral lines). Main improvements were achieved in terms of robustness and stability of the method. Phase correlation method was used to mathematically investigate the thermal shift of the echellogram on the detector and its influence on classification accuracy was also estimated. Considerable effort was also invested in the study of area (its smallest possible size) surrounding each spectral peak (position of local maximum in detected intensity) in the image to yield robust and sensitive analysis.

Presented results suggest feasibility to directly detect selected pixels on intensified detector and thus to overcome conventional utilization of typical line spectrum (intensity vs. wavelength) in certain applications of LIBS technique.

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## *LIBS & Raman Session*

*(Tue. 13<sup>th</sup> of June, h. 11.15-13.00)*



## Miniature Spatial Heterodyne Spectrometers for Remote LIBS and Raman Spectroscopy

S. Michael Angel\*, Patrick Barnett, and Ashley Allen

<sup>A</sup>Department of Chemistry and Biochemistry, The University of South Carolina Columbia, SC 29208 USA

\*smangel0@mailbox.sc.edu

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**ABSTRACT:** We are investigating remote LIBS and Raman spectroscopy using miniature spatial heterodyne spectrometers (SHS) for planetary exploration. The SHS is a dispersive interferometer that offers high optical throughput and high spectral resolution, and it is amenable to miniaturization. In recent work, a SHS was used for standoff laser-induced breakdown spectroscopy (LIBS) measurements. In the described SHLS system the collection aperture was defined by the 10 mm diffraction gratings in the SHS. Standoff LIBS measurements were made with this system up to 20 m with no additional collection optics, corresponding to a collection solid angle of 0.2 micro-sr, or f/2000, using a 130 mJ/pulse 532 nm laser. The ability to miniaturize a SHS Raman spectrometer (SHRS) was recently demonstrated using a standard cell-phone's built in CMOS camera and imaging optics, with 2.5 mm sized diffraction gratings in the SHRS. A similar SHRS system is being used for remote Raman spectroscopy for sample distances up to 10 m. One long-range goal of our studies is to develop remote SHRS and SHLS spectrometers that are compatible with CubeSat architectures, which are made up of 1U units of 10×10×10 cm. To achieve this goal several components of the spectrometer will need to be greatly reduced in size and weight compared to traditional instruments. An overview of these systems will be presented along with a discussion of the potential for further miniaturization.

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## NanoLIBS and its applications

Ken Li\*

B&W Tek Inc., Newark, DE 19713 USA

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*ABSTRACT: We will present a variety of real world applications for our NanoLIBS handheld LIBS spectrometer, including detection of mineral deficiency in biological tissues, identification of pharmaceutical salts, sorting of metal alloys, analysis of glass pharmaceutical bottles, etc. The NanoLIBS employs a micro diode-pumped Q-switched solid-state laser with a high repetition rate of well above 1 kHz in comparison to 1-10 Hz repetition rate lasers as used in a traditional LIBS instrument. The laser beam is fast scanned over a pre-defined area, hence generating several thousands of micro-plasma emissions per second at different locations. Synchronized miniature CCD array spectrometer modules measure these thousands of micro-plasma emissions to produce a LIBS spectrum. By integrating the intensity of this plurality of micro-plasma emissions, the signal-to-noise ratio (SNR) of the obtained LIBS spectrum can be greatly improved. This unique feature of the high repetition rate laser based LIBS system allows it to measure elements at trace levels, hence reducing the limit of detection (LOD). In addition, the energy of the individual laser pulse can be reduced in comparison to traditional LIBS system to obtain the same signal level, making the laser pulse less invasive to the sample.*

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# Laser-ablation alteration of iron sulfides studied at different simulated planetary conditions by Raman spectroscopy

J. Alsemgeest<sup>A</sup>, S.G. Pavlov<sup>B</sup>, S. Schröder<sup>B</sup>, U. Böttger<sup>B</sup>, I. Weber<sup>C</sup>, A. Greshake<sup>D</sup>, H.-R. Knöfler<sup>D</sup>, U. Altenberger<sup>E</sup> and H.-W. Hübers<sup>B,F</sup>

<sup>A</sup>Present address: Van Merodestraat 15, 5271HP, Sint Michielsgestel, the Netherlands

<sup>B</sup>Institut für Optische Sensorsysteme, Deutsches Zentrum für Luft- und Raumfahrt, Rutherfordstraße 2, 12489 Berlin, Germany

<sup>C</sup>Institut für Planetologie, Westfälische Wilhelms Universität, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany

<sup>D</sup>Museum für Naturkunde, Invalidenstraße 43, 10115 Berlin, Germany

<sup>E</sup>Institut für Erd- und Umweltwissenschaften, Universität Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam-Golm, Germany

<sup>F</sup>Institut für Physik, Humboldt-Universität zu Berlin, Newtonstraße 15, Berlin, Germany

**Introduction:** Complementary Laser-Induced Breakdown Spectroscopy (LIBS) and Raman spectroscopy have a high potential for in situ geochemical and mineralogical analyses for planetary exploration. LIBS obtains elemental composition, whereas Raman spectroscopy provides information on the molecular structure and thus can be used for the determination of the mineralogy of geological samples as well as identifying organic and biogenic material. These techniques are highly synergetic and can be integrated into a single compact instrument that can share hardware components as the laser, spectrometer, light-collecting optics, and pointing/focus mechanisms. Combined LIBS-Raman instruments for investigation of, i.e., Mars and Venus surfaces have been proposed in a number of studies (e.g., [1]–[3]). A combined LIBS-Raman instrument, SuperCam, for remote (a few meters) analysis on Mars is currently being developed for NASA's Mars 2020 mission [4].

The LIBS plasma can reach temperatures over 10k K and is accompanied by a plasma shock wave that might alterate the measured minerals, which are then captured by Raman spectroscopy. In addition, specific changes can be associated with Raman laser irradiation [5]. Therefore, when LIBS and Raman spectra are collected successively from the same location, the analysed material can undergo phase changes. Here, we present studies of LIBS ablation-caused alteration of iron sulfides in different atmospheric conditions analyzed by subsequently taken Raman spectra.

**Experiments:** The investigated samples were made from natural minerals, pyrite (FeS<sub>2</sub>, origin: Spain) and pyrrhotite (Fe<sub>1-x</sub>S, Kola Peninsula, Russia), and had optically polished upper surfaces. They were shot with a LIBS pulsed 1064 nm Nd:YAG laser with 50 pulses at a power of 4.9 mJ (pulse duration ~5 ns) focused on a ø 400 µm spot size on the sample's surface. The space-relevant conditions (for Mars: premixed gas at 7.0 mbar; 1 bar of Martian-like gas mixture and for atmosphereless: vacuum) have been simulated in a dedicated chamber. The produced craters have been analyzed by optical- and Raman microscopy afterwards, using a cw laser at 532 nm with a laser power of 1.0 mW. The atmospheric conditions have been kept constant over both LIBS- and Raman measurements. The chamber remained sealed between LIBS and Raman measurements in order to avoid interaction with the Earth's atmosphere.

**Results:** In all measurements, craters were produced with a sharp, central depression reaching up to 44 µm in depth. Ablated volumes ranged from 1.2–1.5 mm<sup>3</sup> for pyrite and 0.5–0.9 mm<sup>3</sup> for pyrrhotite. In the LIBS spectra, emission lines were found for Fe (origin: pyrite and pyrrhotite), Ti (pyrite), Cu and Ni (pyrrhotite) and K and H (pyrite and pyrrhotite, traces). The typical plasma temperature of about 10380 K (±3500 K) has been estimated on the base of the Boltzmann distribution for iron emission lines. In the Raman data, all craters showed a zone of ø1.5–5 mm with spectral changes; although the typical Raman spectra of pyrite and pyrrhotite were still visible, additional peaks were found. This was mainly seen in the outer parts of the zone, where a thin film has been deposited. In vacuum and martian atmospheric conditions at 7 mbar, this film consists of polysulfides, whereas it consists of magnetite after performing LIBS in martian atmosphere at 1 bar. Elemental sulfur is found on the pyrite sample measured in all atmospheres; most dominant for martian atmospheric conditions.

**Conclusions:** The results show that LIBS causes fractionation and reaction of sulfur in both minerals. As the effect appears to be larger with pyrite, heat from the LIBS plasma may be the main driver of this reaction ([6], [7]); this could cause pyrite to react to pyrrhotite and sulfur. Minerals containing other volatiles (i.e., water) are expected to react as well, meaning that possible effects should be taken into account with the interpretation of post-LIBS Raman data from the same spot.

## References:

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## Nuclear Forensics Analysis by Combined LIBS and Raman Spectrometry.

Bobby Bhatt<sup>A\*</sup>, Alix Dehayem- Massop<sup>A</sup>, Kalambuka Hudson Angeyo<sup>A</sup>,

<sup>A</sup>Department of Physics, University of Nairobi, P.O. Box 30197-00100, Nairobi-Kenya.

\*bobby.bhatt@students.uonbi.ac.ke

*Abstract: Nuclear forensics (NF) is the analysis of intercepted illicit nuclear and radiological materials (NRM) so to establish the relationship between NRM and their attribution to monitor nuclear security and proliferation. The critical challenge in NF currently is the lack of suitable microanalytical methodologies for direct, rapid and minimally invasive detection and quantification of NF signatures. Combining Laser Induced Breakdown Spectroscopy (LIBS) and Laser Raman Spectromicroscopy (LRS) can achieve this task particularly when the materials are of limited size. LIBS fingerprints the element associated with the spectral peaks when a powerful laser is focused on a sample surface while LRS uniquely identifies specific chemical compounds and microstructure in a given sample based on molecular vibrations following little or no sample preparation. Although these techniques have potential to identify and quantify at stand-off distance the elemental and molecular composition of NRM, their practical utility is limited by the complexity of the spectra in air at atmospheric pressure and the interpretative challenges of the multivariate data. This paper reports the results we have so far obtained in utilizing LIBS and LRS combined with machine learning (ML) techniques in order to increase their utility towards direct, rapid NF analysis and attribution. We ablated pellets spiked with trace quantities of uranium in cellulose (to mimic uranium hidden and trafficked in an organic matrix) to investigate uranium lines that could be detected in air at atmospheric pressure. U II 385.464 nm, U II 385.957 nm and U II 386.592 nm were identified as the most prominent NF signatures of uranium for rapid qualitative detection of trace uranium in uranium ore surrogates. Principal Component Analysis (PCA) on LIBS spectra successfully classified samples prepared by spiking uranium trioxide in cellulose into uranium and non-uranium bearing. PCA was also performed on LIBS spectra of uranium-bearing mineral ores namely high background radiation area (HBRA) soils (North Ruri, Magadi, Coast) and carbonatite rocks (South Ruri, Magadi, Meru, Coast) from Kenya. The clustering of the samples related the groups to their geographical origins based on REE (viz Dy, Ho, Pr, Pm, Sm and Ti). A multivariate calibration strategy for the quantification of uranium in the soils and rocks was developed using artificial neural network (ANN) (feed forward back-propagation algorithm) utilizing spectral feature selection making use of (i) all the detected uranium lines, (ii) resonant uranium lines with interference (iii) subtle uranium peaks (to demonstrate the power of ANN to model noisy LIBS spectra for trace quantitative analysis). We observed that the calibration model utilizing subtle uranium peaks had the best prediction power of  $R^2 \approx 94\%$ , among the three. The three calibration models were validated using pellets prepared from certified reference material IAEA-RGU-1 with the relative error prediction (REP) ranging between 6 -20 %. The developed calibration model predicted uranium concentrations in the uranium-bearing mineral ores to be in the range 100 ppm - 1771 ppm. In order to understand the various molecular bands associated with the uranium, pellets of uranium compounds (uranium trioxide, uranyl nitrate, uranyl sulphate and uranium chloride, bound in cellulose) were analyzed using multi-photon laser ( $\lambda = 532 \text{ nm}$ ,  $785 \text{ nm}$ ) LRS. NF signatures of uranium trioxide, uranyl nitrate, uranyl sulphate and uranium chloride were identified at  $848 \text{ cm}^{-1}$ ,  $865 \text{ cm}^{-1}$ ,  $868 \text{ cm}^{-1}$  and  $861 \text{ cm}^{-1}$ . These molecular signatures were utilized to infer the presence of uranium compounds in the various HBRA soils. Raman bands associated with uranium molecule were observed at  $844 \text{ cm}^{-1}$  and  $874 \text{ cm}^{-1}$ . Spectral imaging was then performed on a pellet spiked with uranium at trace levels in cellulose (to mimic uranium trafficked in concealed condition) to identify the distribution of uranium in the pellet. It may be concluded that while LIBS is able to detect and quantify uranium in the uranium-bearing mineral ores besides attributing the mineral ores to their geographical origins, LRS identifies the molecular bands associated with uranium occurrence in these minerals and further maps the distribution of uranium through the different surface layers. LIBS and LRS coupled with ML techniques have therefore utility in the detection of uranium in NRM rapidly under concealed condition without destroying sample integrity.*

## Avantes spectrometers for LIBS and Raman applications

Klaas Otten\*

Avantes BV Oude Apeldoornseweg 28 NL-7333 NS APELDOORN The Netherlands, Europe.

\*info@avantes.com

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*ABSTRACT: A typical detection limit of LIBS for heavy metallic elements is in the low-PPM range. LIBS is applicable to a wide range of sample matrices that include metals, semiconductors, glasses, biological tissues, insulators, plastics, soils, plants, soils, thin-paint coating, and electronic materials.*

*Several customers have integrated Avantes spectrometers in different analysers for industrial and laboratory applications. In this presentation we will tell you more about the applications and possibilities.*

*Avantes has some great advantages in LIBS applications:*

- *Multirack in combination with resolution*
- *Timing and triggering*
- *Fast measurements*
- *Purged optical benches*
- *Platform for Hand-held portable*
- *Extensive knowledge on LIBS*

*Raman spectroscopy is especially useful for product identification, reaction monitoring, remote sensing and any other applicable measurement. It provides an invaluable analytical tool for molecular finger printing as well as monitoring changes in molecular bond structure (e.g. state changes and stresses & strains).*

*Avantes uses the high-sensitivity AvaSpec spectrometers in combination with a wide variety of lasers (including 532, 633 and 785 nm) to give you the best result for your Raman measurements. The spectrometers are appropriately configured according to the wavelength of the laser.*

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## Combining Raman and Laser Induced Breakdown Spectroscopy by Double Pulse Lasing

V.N. Lednev<sup>A,B</sup>, P.A. Sdvizhensky<sup>A</sup>, M.Ya. Grishin<sup>B,C</sup>, A.N. Fedorov<sup>B</sup>, S.M. Pershin<sup>B</sup>

<sup>A</sup>National University of Science and Technology MISIS, Moscow, Russia

<sup>B</sup>Prokhorov General Physics Institute, Russian Academy of Sciences, Moscow, Russia

<sup>C</sup>Moscow Institute of Physics and Technology (State University), Dolgoprudny, Russia

vasilylednev@gmail.com

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**ABSTRACT:** A new approach combining Raman spectrometry and laser induced breakdown spectrometry (LIBS) within a single laser event was suggested. A pulsed solid state Nd:YAG laser running in double pulse mode (two sequential nanosecond laser pulses with dozens microseconds delay) was used to combine two spectrometry methods within a single instrument (Raman/LIBS spectrometer). First low-energy laser pulse (power density far below ablation threshold) was used for Raman measurements while second powerful laser pulse creates the plasma suitable for LIBS analysis. The short time delay between two successive pulses allows measuring LIBS and Raman spectra at different moments but within a single laser flash-lamp pumping. The feasibility of combined Raman and LIBS spectrometry measurements was demonstrated for quantitative analysis of solid samples. A tablets of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), anhydrite ( $\text{CaSO}_4$ ) and acetylsalicylic acid powders with two elemental additives (nickel and copper sulfates) were prepared as a reference samples for calibration curve construction for combined Raman and LIBS measurements. Combination of reversed order of laser pulses (first pulse for LIBS and second pulse for Raman measurements) within a single instrument was suggested for remote depth profiling analysis or identification of samples hidden by non-transparent cover (dust, plastic packing, etc.).

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*Industrial Applications Session*  
***Industrial I***

(Tue. 13<sup>th</sup> of June, h. 9.15-10.45)



## A comparative study of LIBS Quantitative analysis of Al alloy using artificial neural networks and calibration methods

Asmaa Elhassan<sup>A,B,\*</sup>, Sabrina M. Aberkane<sup>C</sup>, Khaled A. Elsayed<sup>D</sup>, Tarek Kayed<sup>D</sup>

<sup>A</sup>Science Dept., Deanship of Preparatory Year and Supporting Studies, Imam Abdelrahman Ben Faisal university, KSA; <sup>B</sup>Higher Institute of Technology 10th of Ramadan ,6th of October branch; <sup>C</sup>Centre de Développement des Technologies Avancées, Baba Hassen, Alger, Algérie; <sup>D</sup>Basic Sciences and Humanities Dept., College of Engineering, Imam Abdelrahman Ben Faisal University, KSA

\*asmaa\_elhassan@hotmail.com

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**ABSTRACT:** A comparative study of LIBS quantitative analysis of Al alloy using traditional calibration curves method and chemometric technique, artificial neural networks (ANN), prediction method of different Al alloy samples was achieved. The calibration curve method is used to quantitatively analyze the laser induced breakdown spectroscopy data that is obtained from the Al alloy samples for the investigated elements Ag, Cu and Al. The intensity of the analyte lines obtained from different samples are plotted against their concentration to form calibration curves. The artificial neural network is trained with a set of input data of known composition Al-alloy samples. The calibration curves method was applied on two different unknown samples to determine the unknown concentration of these elements while the trained neural network is used to predict the elemental concentration from the test spectra for the same unknown samples. By comparing the two results of the different analytical methods, ANN method was better than the calibration curves method in the quantitative analysis of Al alloy in terms of accuracy, precision, and limit of detection.

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## Non-ferrous slag analysis using Laser-Induced Breakdown Spectroscopy (LIBS).

Elise François<sup>\*a</sup>, Odhisea Gazeli<sup>b,c</sup>, Stelios Couris<sup>b,c</sup>, George Angelopoulos<sup>d</sup>, Annelies Malfliet<sup>a</sup>, Bart Blanpain<sup>a</sup>

<sup>a</sup>Department of Materials Engineering, KU Leuven, 3001 Heverlee, Belgium;

<sup>b</sup>Department of Physics, University of Patras, 26505 Patras, Greece;

<sup>c</sup>Institute of Chemical Engineering Sciences, Foundation for Research and Technology-Hellas (ICE-HT,FORTH);

<sup>d</sup>Department of Chemical Engineering, University of Patras, 26505 Patras, Greece.

\*elise.francois@kuleuven.be

**ABSTRACT:** Laser-induced breakdown spectroscopy (LIBS) is a promising analytical technique for the on-line analysis of pyrometallurgical process streams, such as metals and slag. Conventionally, the composition of the process streams is measured off-site using XRF or spark-discharge optical emission spectroscopy (OES). However, these procedures are time-consuming. The process control can be improved when real-time information is available. LIBS is therefore an appealing technique due to its fast and remote analysis ability.

In the present study, the LIBS technique is employed for the analysis of synthetic non-ferrous slags, mimicking Cu-slags. The samples will be used for calibration and the analysis of the chemical matrix effect typically occurring in slag samples. Slag samples with different compositions were synthesized using chemical powders. Major elements are Fe, Si, Al and Zn, whereas Cu, Sn and Pb are present in lower concentrations. The powders were homogenized with ethanol using a Turbula mixer and dried in a rotary evaporator. In a first step, the powder mixes were pressed to pellets and analyzed using LIBS. Subsequently, they were melted in an induction furnace at a temperature of 1250 °C using an alumina crucible. While the samples were in molten state, the surface was analyzed using LIBS. A Q-switched Nd:YAG ( $\lambda = 1064$  nm, repetition rate = 10 Hz, max. energy = 450 mJ, pulse width = 5 ns) was used to induce the plasma on both the solid as well as molten samples. The plasma emission was collected by means of a collection optical system and a fiber optic cable and was introduced to a spectrograph equipped with an ICCD detector. The optimal delay time, gate width and suitable emission lines were determined from the analysis of both the solid and molten slag LIBS spectra. A comparison is made between the analysis of the powders and the molten samples. As a first calibration method, the variation of the intensities of the emission lines were plotted as a function of the known concentration. However, since the composition of slag varies considerably, the chemical matrix effect has to be taken into account. Therefore, multivariate statistics were used as a second calibration method, i.e. partial least squares. The method takes into account the complete measured spectra, resulting in a more robust outcome and reducing the matrix effect.

## FTIR PM-IRRAS Spectroscopy and AFM Investigations of Polymer and Copolymer Thin Films Adsorbed on Metal Substrates

Maurice Brogly\*<sup>A</sup>, Diane Fischer<sup>A</sup>, Sophie Bistac<sup>A</sup>

<sup>A</sup>LPIM, Université de Haute Alsace, Mulhouse, France

\*maurice.brogly@uha.fr

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**ABSTRACT:** *The presented works will focus on the understanding on how crystallinity of thin polymer films (either homopolymers or copolymers) is modified in thin films and how this organization can be directed by the surface chemistry of the metal substrate. Various polymers and copolymers were adsorbed by spin-coating on metal substrates. The surface chemistry of the substrates was controlled by chemical grafting using thiols. The influence of the hydrophilic or hydrophobic nature of the substrate on the organization and structuration of polymers and copolymers of different compositions was then studied. Characterization of thin films of polymers and copolymers requires the use of specific characterization techniques. Polarization-Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS) spectroscopy is an innovative and original vibrational spectroscopy that was used for "in situ" reflectivity experiments to characterize thin films of polymers and copolymers deposited on reflective substrates. Due to the polarization modulation of the incident IR wave, its reflection at the interface according to surface selection rules increases the sensitivity of the spectral response, allowing determination of molecular orientation and structuring effects. Atomic Force Microscopy (AFM) analyses were also performed on the same thin films, in order to access the surface morphology and to distinguish the amorphous and crystalline phases. Chains orientations and conformations as well as surface morphologies were thus characterized in order to understand the competition between polymer/polymer and polymer/substrate interactions, which will have a direct effect on the crystallization. This was explained by changes in the balance of polymer/polymer vs polymer/substrate interactions. Substrate surface chemistry alters the balance between these interactions significantly. As an example, in the case of amphiphilic diblock copolymers, a hydrophilic substrate favors the crystallization of the polar block whereas a hydrophobic substrate will favor the non-polar block crystallization. The modification of the crystalline phase content, morphology and molecular orientation of the crystalline structures of the adsorbed films reflects the strong competition between interfacial forces and intra and intermolecular forces.*

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## Automated LIBS sorting system for spent refractories from the steel industry for high-value recycling

Sven Connemann<sup>\*A</sup>, C. Fricke-Begemann<sup>A</sup>, R. Noll<sup>A</sup>, H. Knapp<sup>B</sup>, L. Horckmans<sup>C</sup>, F. Bouillot<sup>D</sup>,  
C. Gehlen<sup>E</sup>, A. Ducastel<sup>F</sup>, A. Stark<sup>G</sup>

<sup>A</sup>Fraunhofer Institute for Laser Technology, 52074 Aachen, Germany;

<sup>B</sup>Unit auf Mineral Processing, RWTH Aachen University, 52064 Aachen, Germany;

<sup>C</sup>VITO, 2400 Mol, Belgium;

<sup>D</sup>ORBIX, 3600 Genk, Belgium;

<sup>E</sup>Laser Analytical Systems & Automation GmbH LSA, 52070 Aachen, Germany;

<sup>F</sup>Magnesita, 59303 Valenciennes Cedex, France;

<sup>G</sup>Tritec-Metal Kft., 6000 Kecskemét, Hungary.

\*sven.connemann@ilt.fraunhofer.de

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*Refractory products are solid ceramic products which are suitable for an application temperature above 1500 °C. Refractory materials are used in a variety of industrial high-temperature processes. The largest consumer of refractory materials is the steel industry, followed by the cement and glass industries. The re-use of refractory material has a high potential to reduce waste production and primary raw material consumption. To allow high-grade recycling and re-use of refractories, efficient separation of the different types of refractory materials based on their chemical composition, combined with an efficient removal of impurities, is essential. The different types are mainly composed of the elements magnesium, aluminium, silicon, calcium and carbon, as well as other materials to improve the properties such as chromium. A fully automated sorting system for whole spent refractory bricks (up to 20 kg) was developed basing on direct chemical analysis of the material using laser-induced breakdown spectroscopy (LIBS). In a joint project of R&D and industrial partners a field scanning LIBS system was used for inline analysis of moving samples in a sorting system which also comprises a feeding unit, a piece singulation unit, a slat conveyor, and a mechanical extraction unit. In order to determine the elemental composition of the different refractory bricks a combination of different LIBS approaches was used. For each measurement a tailored laser pulse train was irradiated on the sample for surface preparation, enabling the penetration of not representative layers. Investigations of the effect of the tailored pulse train on sample surfaces with respect to ablation and laser-material-interaction processes will be presented. As the composition of used bricks can deviate locally, several selected surface locations were evaluated within less than a second to obtain a high representativeness of the classification. Using a multi-CCD spectrometer several spectral lines of each element, which is required for the distinction of the different types of refractories, were recorded simultaneously and evaluated. It has been demonstrated in experiments on an industrial scale that the three main classes of refractory material can be distinguished efficiently.*

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## Rapid measurement system for concrete sample by using laser-induced breakdown spectroscopy

S. Eto\*, T. Fujii

Central Research Institute of Electric Power Industry, 2-6-1 Nagasaka, Yokosuka, Kanagawa, 240-0196 Japan

\*eto@criepi.denken.or.jp

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**ABSTRACT:** A rapid and quasi non-destructive system for the measurement of a cylindrical concrete sample, called as a concrete core and picked out from the reinforced concrete structure, by laser-induced breakdown spectroscopy (LIBS) was developed. The system was composed of a mechanical device to rotate a concrete core and a co-axial LIBS configuration to measure the surface of a concrete core with curvature. Chloride ion concentration is one of the most important factor for the chloride damage of a reinforced concrete. In general, the chemical analysis (potentiometric titration) is used for quantification of chloride ion concentration. However, the potentiometric titration requires a preprocessing of the concrete core and needs a long time to quantify the chloride ion concentration. On the other hand, laser-induced breakdown spectroscopy (LIBS) enables the rapid evaluation of chloride ion concentration because it can measure the chemical composition in concrete without sample preprocessing. Recently, a portable device to survey the surface of the concrete structure have been developed by other groups. The rapid measurement and the quantitative accuracy are important for the application of LIBS to the deterioration diagnostics of the concrete structure. The inhomogeneity of the chemical composition in concrete should be considered carefully for the quantitative accuracy of the chloride ion concentration because the variabilities of emission intensity at each measurement position affect the measurement accuracy of harmful elements such as chlorine and sulfur. We evaluated the chloride ion penetration, by using the diffusion model of chloride ion in concrete, and the carbonation of mortar, by using the linear regression of the relationship between the carbon and the calcium emission intensities obtained by the two-dimensional composition mapping. We developed a rapid measurement system specialized for a cylindrical sample, called as concrete core, which is usually picked out from the reinforced concrete structure. The system enables the quasi non-destructive measurement of the concrete core because the laser pulses is irradiated at the circumference of the sample and the cutting or grinding of the sample is not required at all. The chloride ion concentration was quantified by using the calibration curve obtained using concrete powder samples containing sodium chloride. The results show that the evaluated values of the chloride ion concentration by LIBS were consistent with that by the potentiometric titration. The depth profile of the chloride ion concentration in the concrete core with diameter of 100 mm was evaluated within one hour using the developed system.

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# *Industrial Applications Session*

## ***Industrial II***

*(Tue. 13<sup>th</sup> of June, h. 11.15-13.15)*

## Three Decades of Double-pulse LIBS: from the first steps in 1987 to modern industry applications

S.M.Pershin<sup>A</sup>, V.N.Lednev<sup>B</sup>

<sup>A</sup>Prokhorov General Physics Institute, Russian Academy of Sciences, Moscow, Russia

<sup>B</sup>National University of Science and Technology MISiS, Moscow, Russia

[pershin@kapella.gpi.ru](mailto:pershin@kapella.gpi.ru)

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**ABSTRACT:** First results of double pulse LIBS experiments were published 30 year ago (S.Pershin et al., *Techn. Laser Phys. Lett.*, **13**(14), 870, 1987). A 14x –fold increasing of the LIBS spectra intensity of Al alloy target was achieved by using Nd:YAG laser (20 ns) double pulse with 24 us interval between its. Then the mechanism of double pulse interaction with specifically details in LIBS modifications such as increasing of spectral lines contrast and ablated mass was proposed and proved [1]. Later [2] the original idea of LIBS line correction was formulated and tested on four components bronze samples for using its in standardless technique. Analytical capabilities of LIBS technique were compared for double pulse plasma induced by Gaussian and multimode beam in terms of precision and sensitivity. It was observed that Gaussian beam sampling leads to improvement of analysis precision while sensitivity was element dependent. The higher intensity for atomic/ionic lines in the plasma spectra was observed for multimode beam sampling due to greater laser pulse energy and larger ablated mass. Finally it was found that the crater depth increases nonmonotonically with each successive pulse of the train. A nonlinear, more than by a factor of six, increase in the depth was detected upon interaction of the second pulse with the target.

1. S.M. Pershin, *Quantum Electronics*, **16**, 2518, (1989)
  2. S.M. Pershin, F. Colao et al., *Laser Phys.* **16**(3) 1-13, (2006)
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## Performance Comparison of Handheld LIBS Analyzer with that of Handheld XRF Analyzer in Composition Analysis and Grade Identification of Metallic Alloys.

Stanislaw Piorek<sup>\*A</sup>

<sup>A</sup>Rigaku Analytical Devices, 30 Upton Drive, Suite 2, Wilmington, MA 01887, USA

\*Stan.Piorek@rigaku.com

**ABSTRACT:** *Technological advancements of recent decade have made possible the design of handheld LIBS analyzers. This development rapidly expanded the use of LIBS especially into field operations such as alloy sorting and analysis, the area traditionally dominated by mature, well established technique of X-ray Fluorescence (XRF). Handheld LIBS analyzer has clear advantage over its rival, Handheld XRF Analyzer, because it can analyze light elements such as lithium (Li), beryllium (Be), boron (B), and can outperform XRF when analyzing aluminum (Al), magnesium (Mg), and silicon (Si). Therefore, the first Handheld LIBS Analyzers were primarily used for analysis and sorting of aluminum alloys in which the light elements are important components. However, continuous improvements in Handheld LIBS indicate that this relatively young technique can also be useful in analysis of other important alloy families such as steels, nickel and cobalt based alloys, brasses and bronzes and titanium based alloys. In this paper we will compare analytical performance of a commercially available Handheld LIBS Analyzer with that of one of the best handheld XRF analyzers by presenting the results obtained with both instruments when used for composition analysis and grade identification of alloys representing different alloy families (Fig. 1). Additionally we will attempt to answer the question whether the two techniques are competing or complementing each other. In our analysis we will also account for such factors as ruggedness, ease of use, speed of analysis, sample condition, as well as the most recent improvements aimed at expanding elemental capabilities of handheld LIBS.*

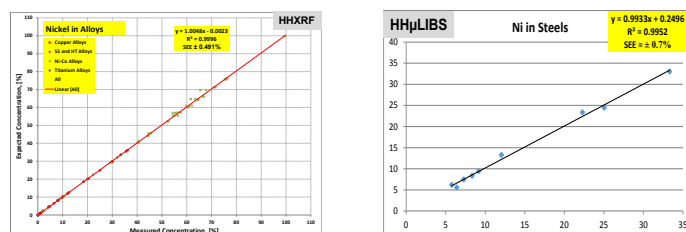


Figure 1. Example of analytical performance for nickel in alloys: HHXRF and HHuLIBS.

## **Abstract Automated contaminant analysis by FTIR microscope**

Jan Knoop\*

<sup>A</sup> Shimadzu Europa GmbH, Analytical BU, 47269 Duisburg, Germany

\*jkn@shimadzu.eu

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*ABSTRACT: With the AIM-9000, Shimadzu provides an analysis systems for all users for quick and easy micro analysis. It targets various industries like electricals and electronics, machinery and transportation, pharmaceuticals and life sciences, petroleum and chemicals and certainly also the food market. Enhanced sensitivity and increased ease enable a complete new user experience.*

*The AIM-9000 offers automation of all necessary steps involved in failure analysis and micro sample evaluation; observation, definition of measurement spots, measurement and identification.*

*A multitude of applications are possible with this highly intelligent platform.*

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## Quantitative analysis of Al-Si alloy using calibration free laser induced breakdown spectroscopy (CF-LIBS)

S. U. Haq<sup>\*A</sup>, Hira Shakeel<sup>B</sup>, Ghulam Aisha<sup>C</sup>, Ali Nadeem<sup>A</sup>

<sup>A</sup> National Institute of Lasers and Optronics (NILOP), P O Box Nilore, Islamabad 45650, Pakistan;

<sup>B</sup> Department of Physics and Applied Mathematics, Pakistan Institute of Engineering and Applied Sciences (PIEAS), P.O. Nilore 45650, Islamabad, Pakistan;

<sup>C</sup> Department of Physics, International Islamic University H-10, Islamabad 44000, Pakistan.

\*sami\_ulhaq2002@yahoo.com

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**ABSTRACT:** The quantitative analysis of standard aluminum-silicon alloy has been performed using calibration free laser induced breakdown spectroscopy (CF-LIBS). The plasma was produced using the fundamental harmonic (1064 nm) of Nd:YAG laser and the emission spectra were recorded at 3.5  $\mu$ sec detector gate delay. The qualitative analysis of the emission spectra confirms the presence of Mg, Al, Si, Ti, Mn, Fe, Ni, Cu, Zn, Sn, and Pb in alloy. The background subtracted and self-absorption corrected emission spectra were used for the estimation of plasma temperature as  $10,100 \pm 300$  K. The plasma temperature and self-absorption corrected emission lines of each element have been used for the determination of concentration of each specie present in alloy. The use of corrected emission intensities and accurate evaluation of plasma temperature yield reliable quantitative analysis with 0.3-2.2% deviation from reference sample concentration

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## Time resolved VUV LIBS for thin film depth profiling.

Syedah Sadaf Zehra<sup>\*A</sup>, John Costello<sup>A</sup>, Paddy Hayden<sup>A</sup>

<sup>A</sup>National Center for Plasma Science & Technology, Dublin City University, Dublin, Pakistan

\*syedahsadaf.zehra@dcu.ie

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*ABSTRACT: Laser Induced Breakdown Spectroscopy (LIBS) is an analytical technique used to classify and potentially quantify elements in complex hosts (or matrices). Vacuum Ultraviolet Laser Induced Breakdown Spectroscopy (VUV LIBS) can offer potential improvements over traditional LIBS in the visible region, due to the abundance of resonance transitions at these shorter wavelengths. This extends the ability to discriminate between the emissions from different elements, particularly light elements such as carbon, sulfur, lithium, and beryllium etc. In addition, as with visible LIBS, the precision obtainable can be limited by the continuum emission at the early stage of the plasma lifetime and greater performance can be achieved by moving to a time resolved detection system, reducing the contribution from the continuum. In this study thin films are being developed to determine the elemental distribution using VUV LIBS for depth profiling, and will be compared to studies previously performed using visible LIBS. Time Resolved VUV LIBS is used for the depth profiling of the thin films and also the limit of detection is compared with respect to Time Integrated Laser induced breakdown spectroscopy for the same samples.*

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## Evaluation of deterioration processes on bricks exposed to industrial-marine environments using field and laboratory analytical methods

Héctor Morillas<sup>\*A</sup>, Cristina García-Florentino<sup>A</sup>, Maite Maguregui<sup>B</sup>, Iker Marcaida<sup>A</sup>,  
Urko Balziskueta<sup>C</sup>, Juan Manuel Madariaga<sup>A</sup>

<sup>A</sup>Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country UPV/EHU, P.O. Box 644, 48080 Bilbao, Basque Country, Spain; <sup>B</sup>Department of Analytical Chemistry, Faculty of Pharmacy, University of the Basque Country UPV/EHU, P.O. Box 450, 01080 Vitoria-Gasteiz, Basque Country, Spain; <sup>C</sup>Department of Geography, Prehistory and Archaeology, University of the Basque Country UPV/EHU, P.O. Box 450, 01080, Vitoria-Gasteiz, Basque Country, Spain.

\*hector.morillas@ehu.eus

**ABSTRACT:** Thanks to the industrialization in the 19<sup>th</sup> century, the use of brick as building material increased and acquired huge importance, being one of the most used construction materials. Usually, the construction bricks are made from clay, which is kneaded with 20-25% water and the resulting paste is moulded and dried at air. Finally the dried paste is fired at about 900–1025°C. Before the firing process, the main components of the raw clay are silicates (e.g. illite-chlorite, quartz, sodium and potassium feldspars, etc.), calcium carbonate (calcite and/or dolomite polymorphs) and iron oxides/hydroxides. During firing, a series of mineralogical transformations are produced, depending on the initial composition of the clay, kiln temperature, heating grade, firing time and prevalence of oxidizing or reducing conditions that affect to the mineralogical composition and microstructure of the final brick. For example, at 900-1025 °C, kaolin is dissociated into silica and alumina and also into calcium silicate and alumina silicate while calcite transforms to CaO. Regarding the physical characteristics of the bricks, the presence of high CaO content in the bricks can cause fissures and cracks when the brick loses the impermeability properties and water goes to the inner part of the brick, reacting with the oxide to form firstly the hydroxide Ca(OH)<sub>2</sub> and subsequently carbonates to form amorphous CaCO<sub>3</sub>. Moreover, this CaCO<sub>3</sub> can react with atmospheric acid gases to form new mineralogical phases (sulphates and nitrates mainly), more soluble than the original CaCO<sub>3</sub>. Bricks included in constructions exposed to marine environments with important anthropic impacts can suffer other more complex chemical processes that conclude in the final destruction of the bricks. In most of the works dealing with the characterization of bricks, the analytical instruments used are benchtop devices. Indeed, there is a lack of works that use hand-held devices to study the conservation state of bricks. In this work, a simple, fast and non-destructive methodology based on the use of hand-held X-ray fluorescence spectrometry was used to perform an in-situ analysis of bricks from Punta Begoña Galleries, a building located in front of the sea (Getxo, north of Spain), with an important atmospheric impact of industrial port, power generation plants and a fuel refinery. The pathologies visually observable in these bricks are disintegration, breakup and detachment. These pathologies are more evident in specific locations and orientations of the construction. In order to extract additional conclusions regarding the orientation of the bricks in the construction, the obtained elemental data matrix was subjected to Principal Component Analysis. In order to confirm and complement these in-situ results, additional analyses were conducted in the laboratory using X-Ray Diffraction and micro-Raman techniques, concluding in the absence of calcium silicate in the most decayed bricks. One of the critical factors in the conservation state of bricks is the content of calcium silicate that provides stability to the structure and resistance to temperature changes, thus the loss of these kinds of silicates (e.g. gehlenite, diopside, etc.) make the analyzed bricks structurally unstable. Moreover, gypsum, a deterioration compound in the bricks, and halite coming from marine aerosol were also identified. Therefore, the molecular and elemental results agree, pointing out to a severe deterioration degree of the bricks used in this historical construction.

## Surface vs. Core analysis of synthetic rubber samples and the influence on the ablation efficiency using LIBS

S. Breithaupt, B. Klie, U. Giese\*<sup>A</sup>

<sup>A</sup>Deutsches Institut für Kautschuktechnologie e.V., Eupener Str. 33, D-30519 Hannover

\*ulrich.giese@DIKautschuk.de

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*The preparation of rubber compounds in the rubber industry is usually carried out in the discontinuous mixing process of the rubber internal mixer. Qualitative differences with regard to the mixing quality achieved, can occur due to batch-induced fluctuations in the raw material, deviations in the mixing process or changes in the ambient conditions from batch to batch. Currently, an evaluation of the mixing quality takes place only after completion of the actual elastomer article or on the vulcanized test piece. Both, a high distributive mixing quality of the mixing components as well as the reduction of the particle sizes of the admixed components (primarily active fillers such as carbon black or silica) are decisive for a good homogeneity of the rubber mixture. The homogeneity of a rubber compound is decisive for the function of a rubber article, since inhomogeneous phases can lead to nonuniform property profiles. The uneven stress of the elastomer article caused thereby can be responsible for a shortened service life and premature component failure. With a practical method for the evaluation of the distributive mixing quality of mixing components, an evaluation of the homogeneity with respect to the material concentrations can be carried out promptly and early component failure can be prevented. Through the introduction of the LIBS method for the analysis of rubber compounds, it is possible to measure the qualitative fluctuations with regard to mixing homogeneity. The flexible design is suitable for both laboratory and continuous production applications. In an online measurement, e.g. directly after mixing, the individual batches can be analyzed and evaluated to determine a possible inhomogeneity of the rubber mixtures. At the German Institute for Rubber Technology (DIK) a LIBS system is installed, which has been specifically adapted to the requirements for the analysis of rubber mixtures with regard to the measurement setup. The results presented in this study deal with the distributive mixing quality of the crosslinking activator zinc (from ZnO) in carbon black filled rubber mixtures. The influence of the particle morphology of the analyte and the filler on the ablation process is investigated with LIBS. To evaluate the distributive mixing quality of the analyte Zn and the signal intensity detected with LIBS, the spectral line at 481.1 nm is used. On the basis of the results, it is clear that the calculated signal-to-noise ratio (SNR<sub>i</sub>) is strongly influenced by the particle morphology of the mixing components. Furthermore, it can be shown that the chemical condition of the sample (analysis of vulcanized vs. unvulcanized rubber samples) as well as the difference between surface and core analysis of the vulcanized test specimen have an influence on the detection limit (LOD).*

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# *Industrial Applications Session*

## ***Industrial III***

(Tue. 13<sup>th</sup> of June, h. 15.00-16.00)



## LIBS for identification and localization of valuable materials in electronic waste

Cord Fricke-Begemann\*<sup>A</sup>, Sven Connemann<sup>A</sup>, Frederik Schreckenber<sup>A</sup>, Reinhard Noll<sup>A</sup>

<sup>A</sup>Fraunhofer Institute for Laser Technology ILT, 52074 Aachen, Germany;

\*cord.fricke-begemann@ilt.fraunhofer.de

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*ABSTRACT: Waste electrical and electronic equipment (WEEE) is known to contain significant amounts of valuable materials. The current recycling technology focusses on the most valuable compounds on an average basis with the consequence that several other compounds are not recovered as it is desirable in a sustainable economic development. Some of the elements currently lost in the industrial processing are considered as strategically important or critical for the European economy. The key for an improvement of the range of recoverable materials is a pre-selection of the components in which they are used which creates a WEEE fraction being enriched in certain compounds. If such a fraction is gained it becomes economically feasible to process it for raw material recovery. To carry out the pre-selection of electronic components on printed-circuit boards (PCB), it is required to first identify the composition the components. LIBS is employed in this work to identify the elemental composition of components on a PCB by a mapping process of the board. Using a 3D galvo scanner, the LIBS measurements can be carried out selectively at all relevant positions with mechanical movement of the samples under investigation. Since the compounds of interest are usually enclosed in a housing, the laser is used for both an ablation process to penetrate the outer shell and for plasma excitation to analyze the interior material. The various elements at each position are revealed and are used to classify the type of electronic component, from which the further processing steps are determined. In this way, for example, tantalum capacitors are identified among a wide range of other SMD components on PCBs from used mobile phones. This provides the basis for automated selective disassembling also using laser technology and metallurgical recovery of valuable raw materials.*

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## **Recent improvements of Echelle spectrographs toward industrial applications.**

David Mory<sup>A</sup>

<sup>A</sup>LTB Lasertechnik Berlin GmbH

david.mory@ltb-berlin.de

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**ABSTRACT:**

- *Recent results of a thermally stabilized spectrometer.*
  - *New detectors are increasing spectral measurement rates; Echelle spectrometers are getting faster.*
  - *Optimization of the optical path - aperture adaptation improves the sensitivity and enables single pulse applications.*
  - *Evaluation of the detector's raw-data significantly improves the reproducibility of measurements*
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## Laser Induced Breakdown Spectroscopy for monitoring laser scribing on organic photovoltaic devices

S. P. Banerjee, Marc Sentis

Aix-Marseille University, CNRS, LP3, F-13288 Marseille, France.

\*banerjee@lp3.univ-mrs.fr

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**ABSTRACT:** The lifetime of an organic photovoltaic (OPV) module can be prolonged if an integrated barrier foil is adapted to the OPV stack. The barrier protects the photosensitive material from the unwanted atmospheric elements such as water vapor transmission. Flexible substrates and much thinner stack construction in OPV's make them more attractive over the conventional inorganic semiconductor solar cells. Laser scribing is needed on the transparent conductive layer, photosensitive organic layer and back electrode layer in order to establish the electrical connections. The protector barrier layer has to be protected from the selective ablation during scribing and a process control needs to set in for monitoring the damage on the barrier layer. Laser Induced Breakdown Spectroscopy (LIBS) retrieves information of the material constituents during ablation and this technique has been applied for this project to develop and monitor the laser scribing process on a multi-layer OPV stack. Two bottom conductive layers (dielectric-metal-dielectric (DMD) with thickness  $\sim 60\text{nm}$  and indium-tin-oxide (ITO) with thickness  $\sim 125\text{ nm}$ ) on the barrier were used. DMD layer is composed of a silver layer sandwiched between two aluminum-zinc-oxide (AZO) layers. The organic layer thickness is  $225\text{-}265\text{nm}$  and the top aluminum electrode layer thickness is  $115\text{ nm}$ . The present work describes mainly the scribing on the organic layer and the possibility of simultaneous LIBS detection. Various laser systems with different temporal widths (nanosecond, femtosecond and picosecond) and different wavelengths (UV, Green and IR) have been applied to check the emission spectra using LIBS. The organic layer is a strong light absorber and the ablation threshold falls in the range of few  $10\text{'s}$  of  $\text{mJ}/\text{cm}^2$  depending on the laser parameters. UV- nanosecond laser pulses were used to identify the possible spectra such as atomic carbon lines and swan bands from the organic layer although selective ablation was not targeted. IR-femtosecond laser pulses were used and LIBS spectra were recorded at different spectral windows to check the spectra from the organic layer. A weak CN band emission was visible. Next, picosecond laser pulses with IR ( $1030\text{ nm}$ ) and Green ( $515\text{ nm}$ ) were used to scribe lines on the organic layer with simultaneous LIBS identification. Different overlapping factors coupled with various energy fluences were applied. The spectra from the bottom DMD layer specifically from the silver was observed at a energy fluence of  $150\text{ mJ}/\text{cm}^2$ . The thickness of the scribed lines were measured using confocal microscopy and it has been demonstrated that the barrier layer was protected during selective ablation. Therefore, LIBS can be accommodated as an analytic tool in an OPV manufacturing unit for process monitoring. Detailed results and discussion will be presented. This project has received funding from the European Commission, Horizon 2020 Research and Innovation Action, in the framework of the ALABO project, Grant agreement No 644026.

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## Laser-induced breakdown spectroscopy for the chemical investigation of concrete infrastructure

Gerd Wilsch\*, Cassian Gottlieb, Tobias Günther, Steven Millar, Nina Sankat

BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany;

\*Gerd.Wilsch@bam.de

**ABSTRACT:** The majority of the built infrastructure is made of concrete, which is a multiphase system made of cement, aggregates, water and pores (every year nearly 4 billion tons of cement are produced which is largest mass flow generated by mankind). Concrete is often used in combination with steel as reinforced concrete. Environmental influences, especially the ingress of harmful ions in combination with the ingress of water, trigger different damage processes which reduce the designed lifetime of a structure. The ingress of chlorides from de-icing salt or sea water leads to corrosion of the reinforcement. Also the carbonation of the concrete may trigger the corrosion of the reinforcement. The ingress of alkalis from de-icing salts may cause the expansion of the amorphous silica aggregates (alkali-silica reaction) through formation of a swelling gel of calcium silicate hydrate if water is present. The ingress of sulfates may cause spalling of the concrete surface due to ettringite formation. For the standard procedure in civil engineering cores are taken, cut in slices, grinded and the obtained homogenized powder is solved in acid and investigated by standard procedures. BAM has developed the LIBS technique for the 2D evaluation of the chemical composition of concrete [1-5]. The technique is established for automated laboratory use with high numbers of samples to investigate transport processes of harmful species (Cl<sup>-</sup>, CO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup> and alkalis) in concrete.

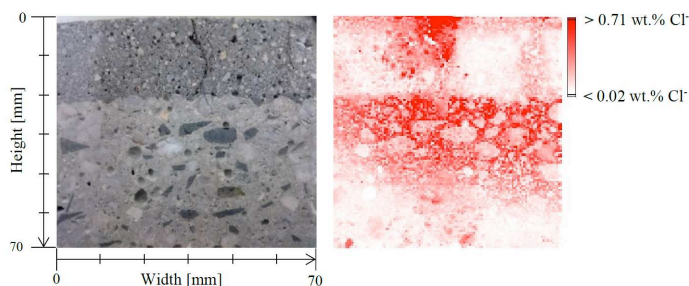


Figure 1: Ingress of chlorides due to a crack in a repair mortar. Left: Photo of the cross section of a concrete core and the surface investigated by LIBS. Right: Color coded chlorine intensity on the cross section of a concrete core, dark red represents high chlorine content.

Information about ingress depth and the quantitative values are important to estimate the remaining lifetime of the infrastructure. LIBS is a surface technique. To get information about the ingress depth, a core has to be taken and cut in the middle. The measurements are carried out at the cross section. The main advantages of LIBS are the direct measurement on the surface of the concrete, fast analysis (sample rate 100 Hz) with a spatial resolution of up to 100  $\mu$ m, the consideration of the heterogeneity of the concrete and the possibility of automated measurements which save a lot of manpower and time.

As an example the investigation of ingress profiles for standard diffusion and migration tests in civil engineering takes hours in comparison to just a few minutes using LIBS. At the same time a 2D-

evaluation provides information about hot spots of elemental concentration which may not be found by standard methods.

The state of the art of LIBS technique for applications in civil engineering will be presented, including typical results of 2D investigation of concrete in laboratory. The performance is also demonstrated by examples for on-site applications using a mobile LIBS system. The road map to standardization is presented as well.

### References:

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# *Biomedical Applications Session*

## ***Biomed I***

*(Tue. 13<sup>th</sup> of June, h. 9.15-10.30)*

## Towards IR-on-a-Chip: Is Smaller Better?

Boris Mizaikoff

Ulm University, Institute of Analytical and Bioanalytical Chemistry, 89081 Ulm, Germany - uni-ulm.de/iabc

\* boris.mizaikoff@uni-ulm.de

**ABSTRACT:** State-of-the-art sensing platforms ideally benefit from miniaturized and integrated optical technologies providing direct access to molecule-specific information. With in-situ sensing strategies e.g., in harsh environments or point-of-care diagnostics in medicine becoming more prevalent, detection schemes that do not require reagents or labeled constituents facilitate localized on-site analysis close to real-time.

However, decreasing the analytically probed volume may adversely affect the associated analytical figures of merit such as the signal-to-noise-ratio, the representativeness of the sample, or the fidelity of the obtained analytical signal. Consequently, the guiding paradigm for the miniaturization of optical diagnostic devices should be creating chem/bio sensing platforms that are as small as still useful, rather than as small as possible, and that smartly capitalize on advantageous features of integrated photonics.

Mid-infrared (MIR; 3–20  $\mu\text{m}$ ) sensor technology is increasingly adopted in environmental analysis, process monitoring and biodiagnostics due to the inherent molecular specificity enabling the discrimination of molecular constituents at ppm-ppb concentration levels in condensed and vapor phase media. Recently emerging strategies taking advantage of innovative waveguide technologies such as substrate-integrated hollow waveguides, and planar semiconductor waveguides shaped into sophisticated optical structures (e.g., MIR Mach-Zehnder interferometers) in combination with highly efficient light sources such as tunable quantum cascade and interband cascade lasers (QCLs, ICLs) facilitate compact yet robust MIR diagnostic platforms for label-free chem/bio sensing and diagnostics. Highlighted applications will include advanced breath diagnostics, mid-infrared assay technology, and IR lab-on-chip systems.

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## Applications of Vacuum Ultraviolet Laser Induced Breakdown Spectroscopy (VUV-LIBS) in the Analysis of Pharmaceuticals.

Paddy Hayden<sup>\*A</sup>, Muhammad Bilal Alli<sup>A</sup>, Syedah Sadaf Zehra<sup>A</sup>

<sup>A</sup>School of Physical Sciences and the National Centre for Plasma Science and Technology, Dublin City University, Dublin 9, Ireland.

\*patrick.hayden@dcu.ie

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*ABSTRACT: As Laser Induced Breakdown Spectroscopy (LIBS) matures as an analytical technique, particularly with the expansion beyond elemental characterization provided by advanced chemometric techniques, the range of potential applications has grown steadily. One such area where the ease of measurement, robustness and accuracy of LIBS can have a significant impact is in the development and production of pharmaceutical and nutraceutical products. While the more usual form of LIBS (utilizing emission in the visible region of the spectrum) may find in-line applications as a Process Analytical Technology to ensure quality control during the final production stages, there are also opportunities for off-line applications for different forms of LIBS to address emerging issues that arise during the development and formulization stages of new products. One such issue at the development stage is that, due to the success of the pharmaceutical sector in expanding their ability to synthesize increasingly complex molecules representing the Active Pharmaceutical Ingredients (API), problems have arisen with traditional models and techniques used to ensure the uniformity of the final product. The API's can tend to crystalize and become localized, and traditional off-line measurement techniques to study this can prove to be extremely time intensive. An important part in the development of new drugs is not just to make new molecules available – but to ensure the required bioavailability and dose is achieved. This presentation will introduce Vacuum Ultraviolet LIBS (VUV-LIBS), utilizing emission in the 35–120 nm range, combined with chemometric techniques, and its usefulness in meeting the off-line requirements at the design stage. A number of advantages, such as increased access to resonance transitions, higher ion stages, less complex spectra, the reduction in non-sample interference effects etc., and disadvantages, such as vacuum requirements, sample damage, resolution etc., will be discussed.*

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## LIBS imaging for supporting medical diagnoses

S. Moncayo<sup>\*A</sup>, B. Busser<sup>A,B,C</sup>, M. Catinon<sup>D</sup>, F. Trichard<sup>A</sup>, M. Sabatier Vincent<sup>B</sup>, F. Pelascini<sup>E</sup>, D. Devismes<sup>E</sup>, N. Pinel<sup>B</sup>, I. Templier<sup>B</sup>, M. Vincent<sup>D</sup>, V. Bonnetterre<sup>B</sup>, J. Charles<sup>B,C</sup>, L. Sancey<sup>C</sup> and V. Motto-Ros<sup>A</sup>

<sup>A</sup> Institut Lumière Matière UMR 5306, Université Lyon 1 - CNRS, Université de Lyon 69622 Villeurbanne, France ; <sup>B</sup> Grenoble University Hospital, F-38000 Grenoble, France; <sup>C</sup> Université Grenoble Alpes, Institute of Advanced Biosciences, IAB INSERM U1209 CNRS UMR5309, F-38000 Grenoble, France; <sup>D</sup> Minapath Développement. Social Busines Society, Villeurbanne, France ; <sup>E</sup> CRITT Matériaux Alsace, 67305 Schiltigheim, France.

[\\*samuel.moncayo@univ-lyon1.fr](mailto:samuel.moncayo@univ-lyon1.fr)

**ABSTRACT:** The presence/absence or dysregulation of endogenous and exogenous chemical elements or agents, particularly metals and minerals, has great interest in various medical specialties. In occupational medicine, for instance, the environmental and occupational exposures to dust or metal agents are responsible of several diseases. However, it is generally hard to diagnose and to correlate the symptomatology with the nature of the agent, the extent and the timing of exposure. This is mainly due to the lack of technology able to detect these agents in a routine way and in a compatible manner with conventional histology. The LIBS imaging performances (speed, resolution, and sensitivity) combined to its all-optical design, make therefore this technology very attractive for medical purposes. Our previous results have boosted the technology to pre-clinical stage in several medical applications, especially in those that the conventional pathology methods do not allow to identify the causative agent. Herein, we address several of these real medical cases. Biopsies from patients with cutaneous inflammatory granulomas are studied with the objective to determine the exogenous material responsible of the inflammation, either metallic allergies after vaccination (Fig. 1), release of metallic species from surgical implants or cutaneous complications linked to ink-tattoo reactions. Biopsies from lung tissue or lymph nodes were also analyzed to explore the link between life-time environmental and occupational exposure to metal agents, and the occurrence of respiratory diseases such as idiopathic pulmonary fibrosis. Finally, we present the feasibility of combining LIBS elemental imaging and histopathological staining procedures to analyze healthy and tumor skin tissues. These results appear promising and may represent the first step towards a more global adoption of LIBS imaging in medical pathology laboratories.

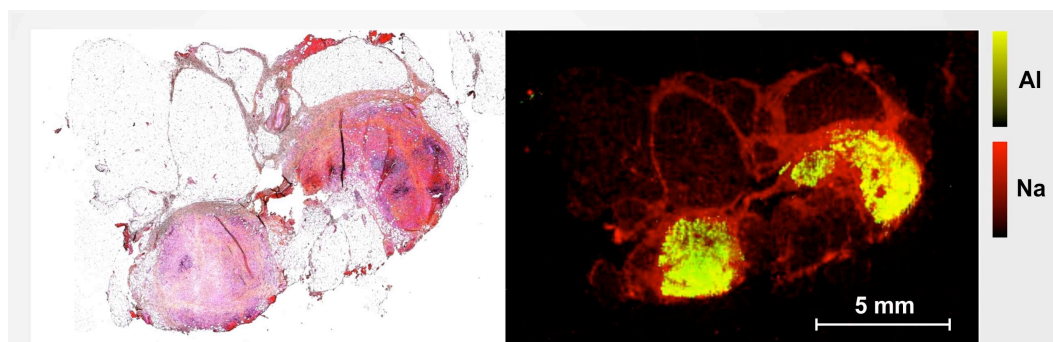


Fig. 1: Images of a human skin granuloma with conventional H&E staining (left), and complementary Bio-LIBS elemental image (right) showing Sodium and Aluminum in red and green, respectively.

## Elemental analysis of the thyroid by laser induced breakdown spectroscopy.

Irfan Ahmed, Condon Lau\*

Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, China

\*condon.lau@cityu.edu.hk

**ABSTRACT:** Thyroid function depends on elements and molecules such as iodine and tyrosine. Iodine and other important elements such as sodium, calcium, iron, are observed in situ and investigated using Laser induced breakdown spectroscopy (LIBS). Along with the sample preparation, LIBS is optimized in both air and argon atmospheres.

**Introduction:** LIBS is an elemental analysis method that uses a high intensity laser pulse to ablate the sample [1]. This leads to an optical emission spectrum that is characteristic of the elements in the sample. LIBS has been applied to study soft tissues [2, 3] such as the kidney, liver, and spleen. In Comparison to other methods of spectroscopy, LIBS offers improved and promising spatial resolution with increased sensitivity even for to lighter elements.

**Methods:** Male Sprague Dawley (SD) rats (N=5, 250–300g) were employed in this study. The SD rates were sacrificed and their thyroids were harvested using surgical procedure. Figure 1(A) show the image of thyroid attached to trachea, while Fig. 1(B) shows the extracted thyroid which were rinsed with saline (0.9 % NaCl) to remove the blood and were immersed in 50 ml test tube containing liquid nitrogen for 20 seconds and then were freeze up to  $-80^{\circ}\text{C}$  for 24 hours before shooting with the laser. The LIBS system employed a 1064 nm pulsed laser (CFR200, Quantel). The pulse was 8 ns in duration. Each pulse focused 200 mJ to a  $10\ \mu\text{m}$  spot on the thyroid. The optical emission from the ablated spot was collected by a seven channel fiber bundle (2000  $\mu\text{m}$  diameter) positioned 3.5 cm from the focus at  $45^{\circ}$  from the laser beam. The fibers relayed light to seven spectrometers (200 – 1000 nm) with 0.1 nm resolution (MX2500+, Ocean Optics). Acquisition occurred 2  $\mu\text{s}$  after laser firing with 1 ms duration.

**Results and Discussion:** From the LIBS spectra in Fig. 2, a number of elements crucial to thyroid function can be observed. These include sodium, iron, and iodine. Spectral lines belonging to carbon, nitrogen, and oxygen are also observed. When argon gas is flowed over the sample at 2.5 L/min (Fig. 2B), the LIBS signal increases considerably as expected and Ar lines can be observed. Increasing the Ar flow rate to 2.5 L/min gives the maximum intensity. The calcium lines appear prominent with the introduction of Ar gas (Fig. 2(C)). The Argon lines measured in Fig. 2(B) are used to calibrate the spectrometer by comparing with the documented wavelengths of the Ar lines from database of National Institute of Standards and Technology (NIST) (see Table 1).

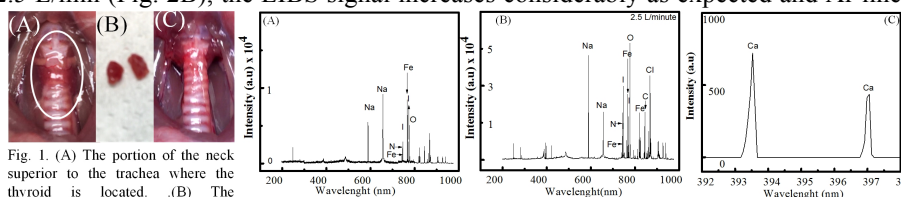


Fig. 1. (A) The portion of the neck superior to the trachea where the thyroid is located. (B) The harvested thyroid sample showing both lobes. (C) The same portion of the neck after the thyroid was removed

Fig. 2. LIBS spectra acquired from rat thyroid samples in air atmosphere (A) and with 2.5 L/min flow of Ar gas over the laser focus spot (B). Calcium peaks are clearly visible with Ar gas (C). Prominent atomic emission lines are labelled. For Ar lines see Table 1

Measured (nm)	696.675	706.871	714.846	727.388	738.458	750.473	763.579	772.477	794.902	Average difference (nm)
Standard (nm)	696.543	706.722	714.704	727.294	738.398	750.387	763.511	772.376	794.818	
Difference (nm)	0.132	0.149	0.142	0.094	0.060	0.086	0.068	0.101	0.084	0.101

Table 1: Calibration of LIBS using Argon spectral lines. The measured Ar lines are from Fig. 2B and the standard lines from NIST database.

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# *Biomedical Applications Session*

## ***Biomed II***

*(Tue. 13<sup>th</sup> of June, h. 11.15-12.30)*

## Microbiological Applications of Vibrational Spectroscopy: Looking inside through the Cell Wall

Alexander A. Kamnev\*, Anna V. Tugarova

Laboratory of Biochemistry, Institute of Biochemistry and Physiology of Plants and Microorganisms, Russian Academy of Sciences, 13 Prosp. Entuziastov, 410049, Saratov, Russia

\*aakamnev@ibppm.ru; a.a.kamnev@mail.ru

**ABSTRACT:** In line with the fast development of biochemistry and molecular biology, in which, within the last decades, modern sophisticated instrumental techniques have increasingly been used, classical basic and applied microbiology also undergoes a revival. It has to be mentioned that microbial metabolic processes, implying compositional and/or structural biomolecular changes in the cell, may be relatively rapid. Therefore, “in situ” and “in vivo” methodologies allowing such changes to be monitored in the intact cell biomass are always preferable to classical (slow) analytical methods. Moreover, separation, isolation and purification of biomaterials from microbial cells can introduce changes in their native structure and/or other properties, not mentioning that these procedures are often laborious and time-consuming. While for biotechnological purposes (e.g. large-scale production of biomaterials of microbial origin) this is inevitable, basic research in microbiology, aimed at understanding the cellular behaviour under certain conditions and responses to external factors, requires information about metabolic processes that take place inside cells within a particular culture. Vibrational spectroscopy techniques (FTIR spectroscopy in various modes; Raman spectroscopy), when skillfully applied, can provide molecular-level information, both structural and quantitative (complementary for FTIR and Raman), on virtually all macrocomponents of the biosystem under study (including intermolecular interactions, which are of paramount importance for most cellular components and their functioning) via analysing experimentally observed vibrational transitions of biomolecular functional groups. In this keynote talk, representative examples will be considered of using FTIR and Raman spectroscopic techniques in microbiological investigations based mainly on our research results on bacteria (see, e.g. [1–5] and references therein), also in addition to other instrumental techniques [2,3,5–7]. The most important issues under study include intracellular accumulation of reserve biopolyesters under unfavourable conditions and their properties in vivo [1,2,4,5]; changes in the secondary structure components of cellular proteins as a response to external factors [4,5]; analysis of bacterial metabolic transformations in the course of selenite reduction to selenium nanoparticles (and their biomacromolecular capping layers) [2]; the formation of bacterial biofilms and their properties as compared to planktonic (freely floating) cultures [1], etc.

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## Vacuum Ultraviolet Laser Induced Breakdown Spectroscopy (VUV-LIBS) For Pharmaceutical Analysis

M. B. Alli and P. Hayden

School of Physical Sciences and NCPST,  
Dublin City University, Glasnevin, Dublin 9, Ireland

muhammed.alli2@mail.dcu.ie

*As an analytical technique, Laser Induced Breakdown Spectroscopy (LIBS) allows quick analysis to determine the composition of the target. Samples need little/no preparation, removing the risk of contamination or loss of analyte [1]. It is minimally ablative so negligible amounts of sample is destroyed, while allowing quantitative and qualitative results [1]. VUV-LIBS [2, 3], due to the abundance of transitions at shorter wavelengths [4], offers improvements over LIBS in the visible region, such as achieving lower limits of detection for trace elements and extends LIBS to elements/samples not suitable to visible LIBS.*

*These qualities also make VUV-LIBS attractive for pharmaceutical analysis. Due to success in the pharmaceutical sector molecules representing the Active Pharmaceutical Ingredients (API) have become increasingly complex.*

*These organic compounds reveal spectra densely populated with carbon and oxygen lines in the visible and infrared regions, making it increasingly difficult to identify an inorganic analyte.*

*The vacuum ultraviolet region poses a solution as there is much better spacing between spectral lines.*

*VUV-LIBS experiments were carried out on Pharmaceutical Samples and Chemometric techniques were applied to analyse the samples [5-7]. The motivation for the application of these Chemometric techniques is the classification of analytes, allowing us to distinguish pharmaceuticals from one another based on their spectra.*

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## The Photoacoustic effect in the field of biomedicine: Imaging, multi-spectral analysis in biomedical applications.

P. Armanetti\*, C. Avigo, A. Flori, L. Menichetti

Istituto di Fisiologia Clinica (IFC), CNR Pisa Italy.

**ABSTRACT:** The laser-induced photoacoustic effect has been recently implemented in biomedical imaging. This effect occurs when a nanosecond laser pulse irradiation is delivered to a tissue which, stimulated by light absorption, produces acoustic waves due to thermoelastic processes. The acoustic waves generated in the tissue could provide molecular information, given by the optical absorption, that can be coregistered with standard ecographic images. The photoacoustic imaging (PA) merges the high contrast, derived from light scattering, with high spatial resolution by ultrasound penetration; this technique works in near infrared region (NIR) and may yields information of endogenous absorbing molecules, like oxy and deoxy form of hemoglobin. The PA can image living organs, giving functional information, such as the blood oxygen saturation, oxy-deoxy haemoglobin ratio, thus giving new insight for angiogenesis and hypermetabolism studies[1],[2]. These characteristics make PA imaging particularly suitable for different kind of studies like the tumor vascularisation microenvironment or the spectral analysis of biological tissue. Currently, PA imaging systems are commercially available; however, there is a lack of reference protocols and test-object specially designed for semi-quantitative evaluation of the performance of a PA system and for the assessment of the contrast enhancement provided by novel materials, under different conditions of excitation wavelength, duration of irradiation, surrounding medium, dilution, and spatial distribution[3],[4]. Although promising biomedical applications are growing for laser-induced photoacoustic imaging, in particular in small animals, the performances of this technique could be better amplified by using proper contrast agents, such as NIR dyes and/or nano-sized constructs: plasmonic metallic nanoparticles are an ideal contrast agent, thanks to their surface plasmon resonance, leading to extinction coefficients that are several orders of magnitude greater than dye chromophores. Indeed, the laser-induced photoacoustic effect stimulates their resonance bands, which can amplify the imaging resolution quality, or convert the contrast agent in a therapeutic – hyperthermic agent[5]. In this field, future work will be devoted to combine laser-induced PA imaging with targeted therapeutic constructs, triggered by near-infrared light or radio-frequency-wave in different model of diseases. you need to replace the text with your abstract.

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## Recent achievements in Life Sciences of the TwinMic soft spectromicroscopy beamline at Elettra

Alessandra Gianoncelli<sup>\*A</sup>, Matteo Altissimo<sup>A</sup>, Diana E. Bedolla<sup>A</sup>, George Kourousias<sup>A</sup>

<sup>A</sup>Elettra – Sincrotrone Trieste, Area Science Park, Basovizza, Trieste, Italy

<sup>\*</sup>alessandra.gianoncelli@elettra.eu

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**ABSTRACT:** The analysis of biological matrices at subcellular level necessitates the use of multidisciplinary techniques and expertise. Soft X-ray Microscopy coupled with spectroscopy can provide insightful simultaneous morphological and chemical information that help in the understanding of biochemical processes taking place at sub-micron scales. In the last few years the TwinMic soft X-ray microscopy station [1] (400-2200 eV) installed at the Elettra synchrotron has been attracting the interests of the Life Science community thanks to its complementary imaging capabilities (brightfield and phase contrast) combined with low energy X-ray Fluorescence and X-ray absorption spectroscopy. Indeed, the developed low energy XRF system [2] enables to correlate the specimen morphology with the elemental distribution of light elements (from B till P) and of transition metals for which the characteristic emission lines fall in the 180-2100 eV energy range. The most recent outcomes in research fields such as neuroscience [3], nanotoxicology [4,5,6], clinical medicine [7,8] and food science [9] will be shown through selected results. The implementation of novel TwinMic imaging modes is in progress and has been recently demonstrated by ptychography with randomly phased illumination acquiring scans across the L absorption edge of iron on fibroblast cells exposed to cobalt ferrite nanoparticles [10] and with phase-diverse Fresnel coherent diffractive imaging of malaria parasite-infected red blood cells [11]. Finally, the current status of ongoing beamline upgrades will be presented including the participation in the development of an advanced X-ray Fluorescence detection system [12].

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## Discrimination of lithiasic components in kidney stones using laser induced breakdown spectroscopy.

Noureddine Cheriet<sup>\*A,B</sup>, Abdelatif Boutenfouche<sup>C</sup>, Sabrina Messaud Aberkane<sup>D</sup>, Samira Abdelli-Messaci<sup>D</sup>, Samia Bouzid<sup>E</sup>, Abderrazek Dahdouhf<sup>F</sup>

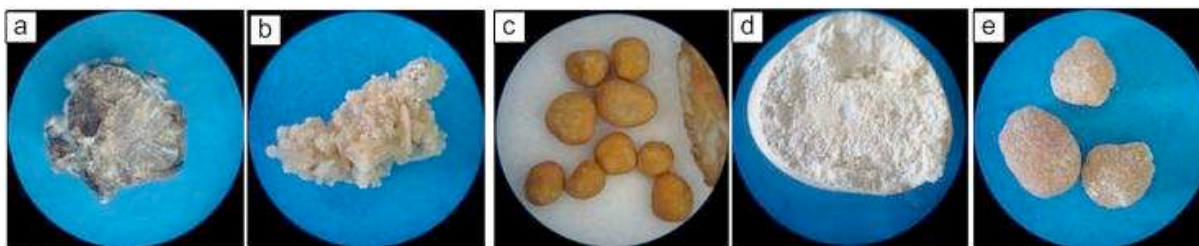
<sup>A</sup>Departement de medecine, Université de Batna2, Algerie; <sup>B</sup>Unité de Recherche Sciences des Matériaux et Applications, Constantine Algerie; <sup>C</sup>Department de medecine, Laboratoire de biophysique, Annaba, Algerie; <sup>D</sup>Centre de développement des technologies avancées (CDTA), Algerie; <sup>E</sup>Departement de physique, Université frères Mentouri, Constantine1, Algerie. <sup>F</sup>EHS d'uro-nephrologie Daksi, Constantine, Algerie

\*n.cheriet@gmail.com

**ABSTRACT:** Kidney stone is the symptom of crystallogenic pathology and metabolic disorders in human body. The determination of stone composition and structure gives specific information about lithogenic conditions involved in its formation and that knowledge is fundamental for establishing the clinical treatment. In this study a set of thirty Kidney stones from the East Algerian region were analyzed from the morphological and composition point of view. Binocular lens (Olympus SZ) for microscopic examination has been used to identify the morphology of stones. The composition of urinary calculi is determined by laser induced breakdown spectroscopy (LIBS) using a Nd-YAG laser at its fundamental wavelength; 1064 nm for the plasma creation. Plasma was collected by an optical fiber of 400  $\mu\text{m}$  and fed onto an echelle spectrometer coupled to the ICCD camera (Aryelle 200 system, LTB -Germany).

The lithiasic components, object of this contribution, are calcium oxalates (with their two crystalline forms whewellite and weddellite (Fig1. a, b), uric acid (Fig1. c), carbapatite, struvite (Fig.1 d) and cystine (Fig.1 e). The spectra obtained by LIBS spectroscopy revealed clear nuances between the different types of these components, thus allowing their characterization by this new analysis technique. Further analysis of these spectra made it possible to identify the specific lines for each type of lithiasic component.

The analysis of urinary calculi by LIBS spectroscopy gave very encouraging results in the identification of lithiasic components. This method can therefore be an interesting and complementary alternative for a more in-depth study of lithogenesis process. Indeed, the low impact of the laser beam used (about 100  $\mu\text{m}$  of diameter) makes it possible to carry out a well localized analysis of any region of stone which makes it possible to determine chronologically the sequences of formation of urinary calculi.



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- <sup>3</sup> Vivek K Singh et al, Quantitative analysis of gallstones using laser-induced breakdown spectroscopy, Applied Optics, 47, 31, 38-47, (2008)

## Characterization of Chiral Drugs by Using Terahertz Time-Domain Spectroscopy

Qicheng Wu<sup>A</sup>, Xin Zhang<sup>A</sup>, Yan Zhang<sup>B</sup>, Yi Liao<sup>A</sup>, Zhuoyong Zhang<sup>\*A</sup>,

<sup>A</sup> Department of Chemistry, Capital Normal University, Beijing, China; <sup>B</sup> Department of Physics, Capital Normal University, Beijing, China.

\*gusto2008@vip.sina.com

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*ABSTRACT: Terahertz Time-Domain Spectroscopy (THz-TDS) has become a novel and powerful analytical tool for the characterization of materials and drugs in chemistry and pharmaceutical industry recently, due to its sensitivity in the field of molecular interactions, the characterization of chiral drugs might be implemented in a convenient approach. In this work, a method of applying THz-TDS with polarized detection has been developed and applied for the characterization and analysis of several chiral drugs and enantiomers. The terahertz absorption spectra of enantiomers were recorded on both horizontal (Ex) and vertical (Ey) directions. Three pairs of chiral reagents, L-camphorsulfonic acid, D-camphorsulfonic acid, (S)-(-)-3-Aminoquinuclidine Dihydrochloride, (R)-(+)-3-Aminoquinuclidine Dihydrochloride, (S)-(+)-1,1'-Binaphthyl-2,2'-diylhydrogen phosphate and (R)-(-)-1,1'-Binaphthyl-2,2'-diyl hydrogen phosphate have been tested. The proposed method shows a feasibility for characterization and analysis of enantiomers.*

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# *Biomedical Applications Session*

## ***Biomed III***

(Tue. 13<sup>th</sup> of June, h. 15.00-16.15)

## Air Bio-Monitoring: a new protocol for cultureless bacteria identification by combining genomic analysis and Raman spectroscopy.

Thomas Signour<sup>A</sup>, Ludovic Duponchel<sup>\*A</sup>

<sup>A</sup> Laboratoire de Spectrochimie Infrarouge et Raman (LASIR, UMR CNRS 8615), Université de Lille, Villeneuve d'Ascq, France.

\* ludovic.duponchel@univ-lille1.fr

*The risk to be exposed to a microbiological contamination always existed, albeit in civil situations (e.g. metro, hospitals or habitats) or in the defense domain (biological weapons, terrorism). To be able to intervene in a safe way, a rapid detection and identification of airborne bacteria is needed. In recent years, spectroscopic techniques, including Raman spectroscopy, have shown great potential for the study of bacteria, moisture and fungi. However, conventional methods for detection and identification of bacteria are known to be time consuming. Therefore, the aim of this work is to find a way to identify cultureless bacteria at the species level, in air samples collected indoors and outdoors, and by means of Raman spectroscopy.*

*Raman spectroscopy is often used in combination with chemometrics to identify bacteria by building a classification model<sup>1</sup>. However, all current studies present relevant models with cultured bacteria and to our knowledge, those models are not robust when they have to predict the identity of a bacterium from a real air sample, as they do not take into account changes the bacteria can suffer in the air. This is why a new protocol is proposed to identify bacteria from a real air sample by combining Raman spectroscopy and genomic analysis, by directly connecting them by means of a NanoGPS which is an absolute repositioning system (Horiba Jobin Yvon). This ensures that the bacteria extracted by Laser Capture Microdissection (LCM)<sup>2</sup> for later single cell genomic analysis are the same as analyzed by Raman spectroscopy.*

*As expected, first results on cultured bacteria show the possibility to discriminate bacteria thanks to Raman spectroscopy using a SVM classification model. In real air samples, an additional difficulty arises as there is a wealth of inorganic particles present, complicating the analysis. A staining of the bacteria is then performed with SYTO9, a green fluorescent nucleic acid stain. It allows us to use the fluorescence of living and dead Gram-positive and Gram-negative bacteria as a discriminatory criterion. Additionally, the use of the ParticleFinder software (Labspec, Horiba Jobin Yvon), allows us to increase the discrimination efficiency by using morphologic parameters of particles. Thanks to these different tools, it is now possible to develop a new protocol allowing us to identify uncultured bacteria from air samples.*

<sup>1</sup> Schmid, U., et al.; Gaussian mixture discriminant analysis for the single-cell differentiation of bacteria using micro-Raman spectroscopy. *Chemom. Intell. Lab. Syst.* **2009**, 96, 159-171.

<sup>2</sup>Emmer-Buck, M., et al.; Laser Capture Microdissection. *Science*. **1996**, 274, 998-1001

## Determination of As, Hg, Mn and Pb in hair using atomic absorption spectrometry as biomarkers of exposure for health risk assessment.

Fiorella Iaquina<sup>\*A,B</sup>; Cristina Álvarez<sup>A</sup>; Paulina Pizzorno<sup>A</sup>; Mariela Pistón<sup>B</sup>; Adriana Cousillas<sup>A</sup>; Nelly Mañay<sup>A</sup>

<sup>A</sup>Área de Toxicología, DEC, Facultad de Química - Universidad de la República, Montevideo, Uruguay; <sup>B</sup>Área de Química Analítica, DEC, Facultad de Química - Universidad de la República, Montevideo, Uruguay.

\*fiaquina@fq.edu.uy

**ABSTRACT:** Arsenic (As), lead (Pb) and mercury (Hg) are the first three elements of The Priority List of Hazardous Substances (ATSDR 2015) due to their frequency, toxicity, and potential for human exposure in contaminated sites. These elements are considered systemic toxicants that induce multiple organ damage and several diseases, ranging from neurological to skin problems, even at low levels of exposure. Other metallic trace elements as manganese (Mn) are essential nutrients required for various biochemical and physiological functions in adequate doses but high concentrations of Mn (above  $3 \mu\text{g g}^{-1}$ ) may cause neurological problems. The determination of the concentration of these toxic elements in hair is useful as biomarkers in screening programs of health risk assessment. Hair can be used as an historical sample, so it is a very convenient sample for chronic exposure assessment. In this work a simple sample preparation method for the determination of As, Pb, Mn, and Hg was developed and validated. Hair samples were taken from healthy non-occupationally exposed adult volunteers. A washing protocol was carried out before sample treatment for hair samples. A microwave-assisted method was employed for hair digestion. 25mg of each sample were digested with 10 mL of  $\text{HNO}_3$  25% v/v and completed to 25 mL with ultrapure water. Analytical determinations were performed by electrothermal atomic absorption spectroscopy (ETAAS) for Pb and Mn, by cold vapor atomic absorption spectrometry (CV-AAS) for Hg and by hydride generation atomic absorption spectrometry (HG-AAS) for As. Detection limits for this matrix were  $0.44 \mu\text{g g}^{-1}$  (Hg);  $1.38 \mu\text{g g}^{-1}$  (Mn);  $1.43 \mu\text{g g}^{-1}$  (Pb) and  $0.28 \mu\text{g g}^{-1}$  (As) using the 3s criteria ( $n=10$ ). Precision was calculated at three levels of concentration (3, 6 and  $9 \mu\text{g L}^{-1}$ ) for each element. For Pb the RSD ranged from 6 to 10%, for Mn between 4 to 6%, for Hg between 5 and 8% and for As between 5 and 7%. Trueness for Mn, Hg and Pb was estimated using a certificate reference material (CRM) purchased from the National Institute for Environmental Studies (NIES) N° 13, Human Hair. Recoveries from the CRM analysis were between 70 and 120% ( $n=8$ ). For As a spike recovery assay was carried out at two levels; this was necessary due to the fact that the certificate value was below the detection limit of this method. The validated method was applied in a presumably environmental exposed children population study. 38 hair samples were obtained following a standard protocol. Results showed that only three of the analyzed samples had Mn levels above  $3 \mu\text{g g}^{-1}$ . Regarding the other contaminants, 6 of them had Pb concentrations considered significantly higher than the mean values expected for non-exposed population. For As and Hg, all samples levels were below quantification limits. A simple analytical method with one single step for sample preparation was successfully applied for the determination of the four elements in hair being very useful for health risk exposure assessment.

## Laser ablation inductively coupled plasma mass spectrometry in elemental imaging of selected mineral and biological samples

Viktor Kanicky\*<sup>A, B</sup>, Michaela Vasinova Galiova<sup>A, B</sup>, Marketa Hola<sup>B</sup>, Tomas Vaculovic<sup>A, B</sup>

<sup>A</sup> Department of Chemistry, Faculty of Science, Masaryk University, Kotlarska 2, 611 37 Brno, Czech Republic; <sup>B</sup> Central European Institute of Technology (CEITEC), Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic.

\*viktork@chemi.muni.cz

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*Abstract: Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) represents a unique technique enabling elemental analysis of solid samples in a wide range of matrices with outstanding detection capability and excellent spatial resolution. These features make it appropriate for analysis of materials where information on local composition and two- or three-dimensional distribution of elements is required. LA-ICP-MS is reported in contribution for study of minerals (mica), biominerals (uroliths, otoliths) and geological samples; moreover, our attention is also paid to soft biological tissues. LA-ICP-MS application in biomedical research, e.g. imaging of tumor tissues, invertebrates, cultivated cells may bring information important for a better understanding of processes in living organisms and can be useful for testing of new potential chemotherapeutics. For selected types of solid matrices, laser ablation-produced aerosol was simultaneously monitored with ICP-MS with fast mobility particle sizer and scanning mobility particle sizer to obtain particle size distribution and its changes depending on laser ablation conditions.*

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## Rapid Malaria Diagnostics via Peak-Free LIBS of Blood

Deborah Musyoka,\* Hudson Angeyo Kalambuka, Alix Dehayem, Kenneth Kaduki

Department of Physics, University of Nairobi, P.O. Box 30197-00100 Nairobi, Kenya.

\*hkambuka@uonbi.ac.ke

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**ABSTRACT:** Body fluids have a unique biochemical composition which alters in response to pathological stimuli. Invasion of pathogens leads to structural and chemical changes as well as the functionality of essential body components. Hence the concentrations, alterations and correlations of trace elements in body fluids can be used as biomarkers for disease diagnosis. Although the spectra contain a lot of chemical information that has relevance in disease diagnostics, LIBS spectra of blood in air and atmospheric pressure are complex and peaks from most trace biometals are optically thick, subtle and undiscernible. By combining peak-free LIBS with multivariate chemometrics (PLS, ANN, PCA) we have achieved accurate quantification of trace Cu, Zn, Fe and Mg in *Plasmodium falciparum* infected blood utilizing the biometals as disease biomarkers. Common optical and clinical techniques of malaria diagnosis which include the gold standard for laboratory confirmation of malaria (examination of stained blood film under a light microscope) are plagued with many shortcomings. We show that the levels of Cu, Zn, Fe and Mg alter predictably during malaria infection and progression of the disease. In order to develop the multivariate calibration strategy for quantitative analysis based on PLS and ANN a model blood was simulated by spiking trace levels of the biometals into a base matrix composed of glycerol, glucose, bovine serum albumin and polyvinyl chloride embedded onto Nucleopore membrane. Oyster tissue was used to delineate the spectral regions of interest (feature selection). NIST/SRM-1598 (inorganic constituents in animal serum) was used to validate the method (accuracy was  $\geq 90\%$ ) for all analyzed biometals. The method was then applied to determine the concentrations of the biometals in malarial blood. Occurrence, concentration and alteration of the biometals in response to *Plasmodium falciparum* infection were determined progressively for 96 hours. The blood was successfully classified as either infected or healthy based on the levels and multivariate correlations among the biometals. The results show that infected blood has higher levels of Cu, and lower levels of Fe, Zn and Mg. The well-known morphological changes of the parasites (merozoites, trophozoites, schizonts) were also successfully determined every 24 hours using PCA indicating that *Plasmodium* infection leads to structural changes that alter the spectra generated in LIBS. We demonstrate that following malaria infection Cu levels increase 328 ppb - 1999 ppb while Fe, Zn and Mg levels decrease 1206 ppb - 674 ppb, 1523 ppb - 499 ppb and 23880 ppb - 19573 ppb respectively. Pearson correlations show that Fe and Cu as well as Zn and Cu have high negative correlation ( $\geq 0.9$ ) in infected blood, while Zn and Cu have high positive correlation ( $\geq 0.9$ ). There is also high negative correlation of Fe and Zn and high positive correlation of Cu and Mg with parasitemia. The results show proof of concept for chemometrics enabled peak-free LIBS as a robust technique for rapid diagnostics of malaria in blood as the LIBS spectra have been ascertained to be a "fingerprint" capable of diagnosis for malaria presence and parasitemia. This is important as malaria is a serious, infectious and widely fatal disease especially in Tropical Africa.

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## Magnetic Resonance Chemical Shift Imaging by hyperpolarized probes: cardiac $^{13}\text{C}$ -spectroscopic imaging of enzymatic fluxes.

Alessandra Flori<sup>A</sup>, G. Giovannetti<sup>A</sup>, MF Santarelli<sup>A</sup>, V. Positano<sup>A</sup>, GD Aquaro<sup>A</sup>,  
L. Landini<sup>A</sup>, L. Menichetti<sup>A</sup>

<sup>A</sup>Istituto di Fisiologia Clinica (IFC), CNR Pisa Italy.

**ABSTRACT:** Dynamic Nuclear Polarization (DNP) [1] and ParaHydrogen-Induced Polarization (PHIP) [2] have recently emerged as a recent method to overcome the Signal-to-Noise Ratio (SNR) limitations in magnetic resonance (MR) - chemical shift imaging (CSI), leading to enhance the nuclear magnetization by several orders of magnitude as compared to the thermal equilibrium signal. Currently, DNP is the most widely used hyperpolarization technique for  $^{13}\text{C}$ -enriched molecules and this enables an increased SNR of  $\approx 10\,000$ -fold.  $^{13}\text{C}$ -MRS allows a semi-quantitative assessment of substrate changes in a target tissue and real-time measurements of metabolic fluxes [3]. CSI with hyperpolarized  $^{13}\text{C}$ -enriched substrates is a promising imaging technique for the evaluation of cardiac metabolism in vivo. Since the natural abundance of  $^{13}\text{C}$  in biological tissue is limited, a sufficient SNR ratio for  $^{13}\text{C}$ -CSI is obtained by increasing the polarization level of these compounds. In this work, different hyperpolarized substances (1- $^{13}\text{C}$ -pyruvate, 1- $^{13}\text{C}$ -acetate and 1- $^{13}\text{C}$ -butyrate) have been investigated in a swine model, to study the typical pattern of distribution of [1- $^{13}\text{C}$ ]-substrates and its downstream metabolites in cardiac tissue.  $^{13}\text{C}$ -CSI is a promising candidate as a novel imaging tool for the evaluation of the regional metabolic changes in the contracting heart: however, many technological improvements are needed to translate this new imaging modality to a clinical application [4].

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# *Materials Session*

## ***Materials I***

(Tue. 13<sup>th</sup> of June, h. 15.00-16.15)

## Model of the interaction of polypyrrole with organic dyes and its influence on polypyrrole morphology – vibrational spectroscopy study.

Zuzana Morávková<sup>A</sup>

<sup>A</sup>Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky sq. 2, 162 06 Prague, Czech Republic.

\*moravkova@imc.cas.cz

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*Polypyrrole (PPy) is one of the most popular conducting polymers due to its good environmental stability and conductivity. Typically, oxidation of pyrrole leads to the granular morphology of PPy. It has been shown lately, that addition of methyl-orange (MO) to the reaction medium where PPy is prepared induces the formation of nanotubular morphology [1]. The formation of nanotubes was explained simply by the formation of solid MO templates in the reaction medium. However, later experiments with deprotonation of PPy–MO nanotubes [2] and the addition of other dyes, such as ethyl-orange, acid blue 25 and acid blue 129, to the reaction mixture, have allowed a more detailed view of the nanotube structure and formation process. All samples were thoroughly studied by Fourier-transform infrared and resonance Raman spectroscopies. These methods, considering their specific sensitivities and depth of penetration, enabled the understanding of the structure of PPy nanotubes, namely of the content of the dye and protonation of PPy at inner and outer side of the nanotube wall. Some dyes lead to the formation of PPy nanotubes (MO, acid blue 25) and some do not (ethyl-orange, acid blue 129). This, and the structure of the PPy nanotubes as observed by vibrational spectroscopies, can be explained by a model based on the changes of pH of the reaction medium during the oxidation of pyrrole together with the solubility of the dye in aqueous media of various acidities. According to this model, dyes that will lead to the nanotubular PPy morphology can be effectively selected. [1] J. Kopecká, D. Kopecký, M. Vrnáta, P. Fitl, J. Stejskal, M. Trchová, P. Bober, Z. Morávková, J. Prokeš, I. Sapurina: Polypyrrole nanotubes: mechanism of formation. RCS Adv. 2014, 4, 1551. [2] J. Stejskal, M. Trchová, P. Bober, Z. Morávková, D. Kopecký, M. Vrnáta, J. Prokeš, M. Varga, E. Watzlová: Polypyrrole salts and bases: superior conductivity of nanotubes and their stability towards the loss of conductivity by deprotonation. RSC Adv. 2016, 6, 88382. The Czech Science Foundation is acknowledged for financial support (project no. 17-04109S).*

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## Mass-charge shift ratio to increase accuracy through oxide formation of Mn, Ni and Fe focusing on their determinations by ICP-MS

Eraldo Luiz Lehmann <sup>a,b</sup>, Marco Aurélio Zezzi Arruda <sup>a,b</sup>

a - National Institute of Science and Technology – INCT for Bioanalytics, Institute of Chemistry, University of Campinas – Unicamp, Brazil; b - Group of Spectrometry, Sample preparation and Mechanization – GEPAM, Institute of Chemistry, University of Campinas – Unicamp, Brazil.

\*zezzi@iqm.unicamp.br

*In this work, the shift of the mass-charge ratio, through oxide formation, was evaluated to improve the accuracy in the determination of Manganese, Nickel and Iron employing an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and the Dynamic Reaction Cell (DRC). The only Mn isotope is  $^{55}\text{Mn}$  and it presents as interferent K; the most abundant isotope of Fe is the  $^{56}\text{Fe}$  (91.72%), and the presence of Ar and Ca interferes on its quantification; the most abundant isotope for Ni is the  $^{58}\text{Ni}$  (68.077%), and this isotope could be interfered by Fe and Ca. In the other hand,  $^{55}\text{Mn}^{16}\text{O}^+$ ,  $^{56}\text{Fe}^{16}\text{O}^+$  and  $^{58}\text{Ni}^{16}\text{O}^+$  present no significant interferences. Gallium also present  $m/z$  as 71 and at  $m/z = 72$  it is possible find Ge; Germanium presents  $m/z = 74$  and also Se; however, the low presence of these elements in Earth Crust (Ga ca. 19 ppm and Ge ca. 1.5 ppm) and their low solubility in diluted acids (such condition is currently found by ICP-MS analysis), denotes the low probability of their interferences. On the other hand, Se is soluble at such conditions, nevertheless, Se is an element with a tendency to form oxide inside the DRC. Then, to propose an alternative for eliminating some polyatomic and/or isobaric interferences already described, the shift of the mass-charge ratio through the formation of the analyte oxide was carried out using a DRC, by filling this cell with a reactive gas ( $\text{O}_2$  in such case) for minimizing/avoiding such interferences. In this way, the best condition was evaluated for generating analyte-oxide species, which involved the  $\text{O}_2$  flow-rate and the Rejection Parameter of quadrupole (RPq), dimensionless value given by Mathieu Equation, which correlates the voltage applied in the rod of the quadrupole and the stability of the ion. The instrument has a tool for the DRC optimization, which involves some variables such as the matrix solution (M) presenting all interferents, and a spiked solution (S), containing the interferent + the analyte. By fixing the gas flow-rate, the RPq value is then varied. These solutions were prepared with all analytes and interferents describe above. For all optimization, the values of the gas flow-rate (GFR) was evaluated from 0.1 to 1.0  $\text{mL min}^{-1}$  and the RPq from 0.4 to 0.9. The best value of GFR and RPq were, respectively, to the wa 0.6  $\text{mL min}^{-1}$  and 0.55 for  $^{56}\text{Fe}^{16}\text{O}^+$  formation; 0.5  $\text{mL min}^{-1}$  and 0.55 for  $^{55}\text{Mn}^{16}\text{O}^+$ ; 0.4  $\text{mL min}^{-1}$  and 0.55 for  $^{58}\text{Ni}^{16}\text{O}^+$ . Analytical curves were obtained at their best condition, and the parameters (slope, linearity, linear range and limit of quantification) obtained were: for Fe 151.78, 0.9973, 1–25  $\mu\text{g L}^{-1}$  and 0.91  $\mu\text{g L}^{-1}$ , respectively; for Mn, 155.65, 0.99927, 1–25  $\mu\text{g L}^{-1}$  and 0.56  $\mu\text{g L}^{-1}$ , respectively; and for Ni, 53.83, 0.99930, 0.5–25  $\mu\text{g L}^{-1}$  and 0.33  $\mu\text{g L}^{-1}$  respectively. Certified reference material of water was employed for accuracy purposes, with recoveries of ca. 100% for each analyte, making this strategy an elegant alternative for accurately determining Mn, Ni and Fe by ICP-MS.*

## **S<sup>2</sup>XAFS: Time-resolved X-ray absorption spectroscopy in a ‘single-shot’ – First in situ applications.**

Anicó Kulow<sup>A</sup>, Ana Guilherme Buzanich\*<sup>A</sup>, Sebastian Beyer<sup>A</sup>, Martin Radtke<sup>A</sup>, Uwe Reinholz<sup>A</sup>,  
Heinrich Riesemeier<sup>A</sup>

<sup>A</sup> Federal Institute for Materials Research and Testing (BAM). Richard-Willstaetter-Straße 11, 12489 Berlin, Germany

\*ana.buzanich@bam.de

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*ABSTRACT: The newly developed EXAFS set-up comprises both time- and spatially-resolved EXAFS information simultaneously in a single-shot. This facile, stable and scanningless set-up was tested at the BAMline @ BESSY-II (Berlin, Germany). The primary broadband beam is generated by a filter/X-ray-mirror combination (bandpass). The transmitted beam through the sample is diffracted by a convexly bent Si (111) crystal, producing a divergent beam. This, in turn, is collected by an area sensitive detector, in a  $\theta - 2\theta$  geometry. The first in situ measurements were successfully carried out and hereby presented. The case-study deals with research on Zn-based Metal-Organic-Frameworks (MOFs) that have potential for medical/pharmaceutical applications. This hot topic of MOF research targets encapsulation of therapeutically relevant biomacromolecules (e.g. Enzymes) for drug delivery applications. Questions regarding the influence of proteins on the coordination of Zn during MOF crystal growth and within the final MOF can be answered with this new setup. We were able to track structural changes within a 1s time resolution.*

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## Application of principal component analysis model for real-time monitoring membrane fouling

Tiina Virtanen<sup>\*A</sup>, Satu-Pia Reinikainen<sup>A</sup>, Jussi Lahti<sup>A</sup>, Mika Mänttari<sup>A</sup>, Mari Kallioinen<sup>A</sup>

<sup>A</sup>LUT School of Engineering Science, Lappeenranta University of Technology, P.O.Box 20, 53851 Lappeenranta, Finland.

\*tiina.virtanen@lut.fi

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*ABSTRACT: Membrane fouling is a critical challenge in membrane filtration processes as it causes a decrease in filtration capacity and might also affect the selectivity of the used membrane. Novel early warning techniques for the detection of fouling problems in membrane processes is needed for improvement of fouling prevention strategies. Normal Raman spectroscopy has been recently applied as real-time measurement tool for the non-destructive monitoring of membrane fouling and cleaning of commercial polyethersulfone membranes. Water solutions of vanillin with different concentrations and pH values were used as a feed solution and adsorption of vanillin on the surface of the membrane was detected by Raman spectroscopy. The results were validated by external calibration method, i.e. extraction and UV-visible spectroscopic analysis. The real-time Raman data was supplied to spectral preprocessing and principal component analysis (PCA). The calibrated data was used to build the PCA model, which presents the membrane process that is proceeding in the desired way. The experimental results showed a fairly good correspondence between the predicted concentrations based on PCA model and actual measured concentrations of adsorbed vanillin. Secondly, the PCA model based technique was successful in monitoring membrane flushing and concomitant desorption of vanillin. The model was also able to differentiate anomalous processes based on differentiating score and loading values. The normal Raman spectroscopy combined with PCA model has potential to be used for monitoring and controlling of fouling and cleaning in membrane processes.*

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## Fingerprint Identification of Inorganic Compounds Using Terahertz Time-Domain Spectroscopy

Lijuan Huang, Xin Zhang, Yi Liao, Zhuoyong Zhang\*

Department of Chemistry, Capital Normal University, Beijing 100048, China.

\* gusto2008@vip.sina.com

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*ABSTRACT: Metal complexes widely exist in our environment and are highly related with human society. Now the characterization of metal complexes is implemented by using XRD (X-ray diffraction), UV (ultraviolet and visible spectrophotometer), FTIR (Fourier infrared spectroscopy), NMR (nuclear magnetic resonance) etc. Terahertz time domain spectroscopy (THz-TDS) provides a novel approach for coordination compounds characterization. In this paper, the THz spectra of the salts of manganese, cobalt, copper and iron and their EDTA complexes were investigated. Comparing to the infrared spectra of these compounds, THz spectra provided more absorption bands for each ion complexed with different ligands. Especially,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  can be distinguished based on the THz spectra, as proposed in this work. The molecular vibration information in the THz wave band provides the fingerprint for further study of coordination compounds identification.*

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## Structure, Vibrational Analysis and Intramolecular Hydrogen Bond Strength of Some 4-Amino-3-Penten-2-One Derivatives

Ali Reza Berenji<sup>\*A</sup>, Sayyed Faramarz Tayyari<sup>B</sup>, Mohammad Vakili<sup>B</sup>, Samira Soltani-Ghoshkhaneh<sup>C</sup>

<sup>A</sup>Department of Metallurgy, Academic Center for Education, Culture, and Research (ACECR), Mashhad 91779, Iran; <sup>B</sup>Department of Chemistry, Ferdowsi University of Mashhad, Mashhad 91779, Iran; <sup>C</sup>Department of Chemistry, Ferdowsi University of Mashhad, International Campus, Mashhad 91779, Iran.

\*berenji@staff.um.ac.ir, aberenji@gmail.com

**ABSTRACT:** 4-Amino-3-penten-2-one (APO) is one of the interesting  $\beta$ -enaminones, involved in the N-H...O intramolecular hydrogen bond system assisted by resonance [1]. This special hydrogen bonding makes them to play the role of a good ligand and to provide useful complexes. To identify the structure and stability of these complexes, the structure and intramolecular hydrogen bond strength of these ligands should be investigated. In this study, the molecular structure and vibrational spectra of 4-butylamino-3-penten-2-one (BPO) and 4-tert-butylamino-3-penten-2-one (tBPO) were investigated using density functional theory (DFT). The geometrical optimization and vibrational wavenumber calculations were performed at the B3LYP/6-311++G(d,p) level. The results were compared with the corresponding experimental infrared (IR) spectra. Fourier Transform IR spectra of BPO and tBPO were clearly assigned. The spectra were also compared with the simplest similar molecule, namely APO [2]. The hydrogen bond strength in all stable structures is estimated by considering the geometrical parameters obtained from the DFT calculations and also by calculating the hydrogen bond energies using Bader's atoms in molecules (AIM) theory. According to our calculations, the N...O distance in BPO and tBPO is 2.664 and 2.666 Å, respectively. It confirms that the hydrogen bond in these molecules are slightly stronger than that in APO (2.671 Å) [3]. The difference between the studied compounds and APO is the substitution of the -NH<sub>2</sub> group by the -NHC<sub>4</sub>H<sub>9</sub> group in APO. According to our study, two factors are responsible for increasing the bond strength, i.e., steric effect and inductive effect. The results obtained from AIM and NBO calculations also confirm the above conclusion. Excellent correlations were achieved between geometrical parameters (except N...O distance), AIM, NBO,  $\gamma$ NH,  $\nu$ NH and  $\delta$ NH with the hydrogen bond strength,  $E_{HB}$ . As an overall result, the hydrogen bond strength of the understudy molecules follows the below order:

tBPO > BPO > APO.

### References

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- [3] A.R. Berenji; S.F. Tayyari; M. Rahimizadeh; H. Eshghi; M. Vakili; A. Shiri. in: A. Afkhami (Ed.). *Book of Abstracts of 15th Iranian Chemistry Congress, Bu-Ali Sina University, Hamedan*, **2011**, p. 1065.

# *Materials Session*

## ***Materials II***

(Wed. 14<sup>th</sup> of June, h. 9.15-10.30)

## Innovations in Spectral Sensing Exploring $\text{Ag}^+$ Coordination Polymers Facilitated by $\text{Ag}^+$ - $\text{Ag}^+$ Interactions

Qian Zhang, Dan-Dan Tao, Dan Liu, Na Chen, Qian Wang, Zhao Li, and Yun-Bao Jiang\*

Department of Chemistry, College of Chemistry and Chemical Engineering, The MOE Key Laboratory of Spectrochemical Analysis and Instrumentation, and iChEM, Xiamen University, Xiamen 361005, China

\*ybjiang@xmu.edu.cn

**ABSTRACT:** While the majority of the chemosensing is realized using individual molecular sensor that bears a binding site for analyte species and a signal reporter, that are linked by a spacer in the structural framework of “Signal reporter-Spacer-Binding site”, we launched a spectral sensing scheme by using metal coordination polymers. We chose  $\text{Ag}^+$ -thiol coordination polymers as our first system to explore. These coordination polymers have been extensively employed as precursors for preparing Ag nanoparticles, yet the polymers themselves have not been understood well. We envisaged to introduce a binding site to the thiol ligand we would be able to create a sensing platform for spectral sensing for those binding to the thiol ligand of much higher local concentration and tunable orientation of the binding sites in the polymers than in the thiol ligand itself, to allow a much better sensing performance. We assumed that metal-metal interactions that have been observed with  $d^{10}$  metal ions such as  $\text{Au}^+$ ,  $\text{Ag}^+$  and  $\text{Cu}^+$  may operate in the coordination polymers as an additional driving force for the formation of the dynamic polymers. We started our exploration first by mixing  $\text{Ag}^+$  and the thiol amino acid cysteine in acidic buffers and we observed absorption and CD signals around 350 nm, which we assigned to the  $\text{Ag}^+ \dots \text{Ag}^+$  interaction related new chromophore. This established a background-free spectral sensing system for cysteine that features a higher sensitivity. We showed by tuning the solution pH and thus the existing forms of the cysteine residue the operation of the  $\text{Ag}^+ \dots \text{Ag}^+$  interactions and the transfer of the chirality of the cysteine residue to the  $\text{Ag}^+ \dots \text{Ag}^+$  interaction related chromophore as a mirror-imaged CD profiles were observed when D- and L-cysteines were respectively employed. We concluded that both the  $\text{Ag}^+ \dots \text{Ag}^+$  interactions and the electrostatic interactions between the cysteine residues contributed to the stabilization of the coordination polymers. Whereas the  $\text{Ag}^+$ -cysteine polymers are weakly fluorescent, the  $\text{Ag}^+$ -GSH polymers are highly fluorescent presumably because of the much stronger interaction among the GSH ligands in the polymers. In support of this assumption we observed the hydrogelation of the  $\text{Ag}^+$ -GSH polymers, which allowed the creation of a highly sensitive and selective sensing scheme for  $\Gamma^-$  that competes to bind  $\text{Ag}^+$  cations and thus the breaking of the gel and the release of much more amount of water entrapped in the gel. This response promoted us to create a new fluorophore-containing cysteine derivative by making the latter into the amide of (2-naphthyl)acetic acid as emission of the naphthalene fluorophore at ca. 350 nm could excite the  $\text{Ag}^+ \dots \text{Ag}^+$  related chromophore to enhance the emission of the polymers, thus the naphthalene fluorophore acting as an antenna. Upon excitation at 280 nm of the naphthalene chromophore in the polymers, we indeed observed emission at both 340 nm and 440 nm, due respectively to the fluorescence of naphthalene and the  $\text{Ag}^+ \dots \text{Ag}^+$  chromophore, allowing a ratiometric fluorescent sensing of  $\text{Ag}^+$ . In the former cases we noted that the CD profiles are the same if the cysteine residue is of the same configuration. We attributed this observation to the inclusion of the chiral centers within the network that includes both the chiral thiol ligand and the  $\text{Ag}^+ \dots \text{Ag}^+$  chromophore because of the aforementioned thiol-thiol interactions. We therefore proposed the general scheme of the spectral sensing of using the  $\text{Ag}^+$ -thiol coordination polymers by introducing a binding site into the thiol ligand. We verified this proposal by introducing a boronic acid group into the achiral benzenetriol for chiral sensing of monosaccharides. The rationale behind is that upon binding to a monosaccharide of the boronic acid the achiral thiol ligand may turn into chiral in particular when monosaccharides such as glucose that could bind to two boronic acid groups the  $\text{Ag}^+ \dots \text{Ag}^+$  chromophore is included within the binding network. We did observe varying CD profiles when a variety of monosaccharides were applied to the  $\text{Ag}^+$ -thiol coordination polymers. These promising preliminary data have ensured our mission of sensing explorations for other species, both achiral and chiral, for which details of recent advances will be presented in my lecture. I thank the financial supports by the NSF of China and the Ministry of Education of China.

## Analysis of Laser Treated CFRP Surfaces by Laser-Induced Breakdown Spectroscopy

Belgin Genc Oztoprak<sup>\*A</sup>, Erhan Akman<sup>A</sup>, Onur Çoban<sup>A</sup>, M. Özgür Bora<sup>A</sup>, Arif Demir<sup>B</sup>

<sup>A</sup> Faculty of Aeronautics and Astronautics, Kocaeli University, Kocaeli, Turkey;

<sup>B</sup> Department of Physics, Kocaeli University, Kocaeli, Turkey.

\*belgingenc@kocaeli.edu.tr

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*ABSTRACT: Carbon Fiber Reinforced Polymers (CFRPs) have been used aeronautical, marine and automotive industry for manufacturing different components since CFRPs have lots of advantageous specification such as high strength, high stiffness, good shear properties, low density and corrosion resistance. Strong joining of CFRPs is applied by using various methods such as adhesive bonding, rivets or bolts. Adhesive bonding has numerous advantages for joining of components when surface is prepared properly. Laser surface treatment is a developing method in preparation the CFRP surfaces. In this study the influence of surface chemistry to the contact angle measurement and adhesive bonding strength of CFRP composites was investigated in the CO<sub>2</sub> laser ablated composite structures. Surface characterization of CFRP samples was carried out using laser induced breakdown spectroscopy with a nanosecond pulsed Nd:YAG laser and an ICCD camera before and after laser treatment. The surface characterization of laser treated carbon fibers was identified C, O, N and several trace elements including Ca, Mg, Na, Si etc.*

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## An innovative spectroscopic technique for the study of palladium behavior in Alkaline Fuel Cells

Walter Giurlani<sup>\*A</sup>, Alessandro Lavacchi<sup>B</sup>, Andrea Giaccherini<sup>A</sup>, Francesco Di Benedetto<sup>C,D</sup>, Giordano Montegrossi<sup>D</sup>, Stefano Freschi<sup>E</sup>, Francesco D'Acapito<sup>F</sup> and Massimo Innocenti<sup>A,B</sup>

<sup>A</sup>Dipartimento di Chimica, UNIFI, via della Lastruccia 3, 50019, Sesto Fiorentino (FI), Italy; <sup>B</sup>CNR-ICCOM, via Madonna del Piano 10, 50019, Sesto Fiorentino (FI), Italy; <sup>C</sup>CNR, Istituto di Geoscienze e Georisorse, via G. La Pira, 4, 50121, Firenze (Italy); <sup>D</sup>Dipartimento di Scienze della Terra, Università di Firenze, via La Pira 4, 50121, Firenze (Italy); <sup>E</sup>Freschi & Vangelisti, Viale Europa 1, 52028, Castel S. Niccolò, Arezzo (Italy); <sup>F</sup>CNR, Istituto di Officina dei Materiali, OGG, c/o ESRF, Grenoble (France).

\*walter.giurlani@unifi.it

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*Alkaline Direct Alcohol Fuel Cells (ADAFc) are particular interesting fuel cells because, in addition to convert chemical energy in electrical energy, could work with cheaper catalyst than platinum and also provide interesting products for industrial application, like acetates. These devices need to be understood in deep to improve their extrinsic energy efficiency. To reach this goal Fixed Energy X-ray Absorption Voltammetry technique have been used. FEXRAV (Fixed Energy X-ray Absorption Voltammetry) and represents an innovative, fast and easy [1] method for the in situ and in operando X-ray absorption analysis at a fixed energy during a cyclic voltammetry and is particularly suitable for the investigation on the electroodic surface for heterogeneous catalytic reactions [2]. For the first time FEXRAV have been used to study the palladium behavior. In particular palladium nanoparticles supported on carbon have been studied in solution of KOH and various organic fuels. By results, it is possible to detect and quantify the percentage of oxide on the catalyst, the maximum overpotential before the poisoning of the catalyst and its loss in function of time; even some information on the reaction mechanisms could be obtained. References:[1] A. Minguzzi, O. Lugaesi, C. Locatelli, S. Rondinini, F. D'Acapito, E. Achilli, P. Ghigna, Anal. Chem. (2010), 85, 7009-7013. [2] A. Minguzzi, O. Lugaesi, E. Achilli, C. Locatelli, A. Vertova, P. Ghigna, S. Rondinini, Chem.Sci. (2014), 5, 3591-3597.*

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## New sonochemically assisted synthesis of structured non-noble catalyst for methane and VOCs combustion

Roman J. Jędrzejczyk<sup>\*A</sup>, Przemysław Jodłowski<sup>B</sup>, Damian Chlebda<sup>C</sup>, Anna Dziejdzicka<sup>B</sup>

<sup>A</sup>The Malopolska Centre of Biotechnology, Jagiellonian University, ul. Gronostajowa 7A, Kraków, Poland; <sup>B</sup>Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 30-155 Kraków, Poland; <sup>C</sup>Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Kraków, Poland

\*roman.jedrzejczyk@uj.edu.pl

**ABSTRACT:** Zirconia with its unique electrical and mechanical properties has drawn interest of the energy related industry, in gas abatement applications<sup>1-2</sup>. Since, the alternative for fossil fuels are on high demand, the application of catalytic combustion to produce the electricity from biogas was proposed and investigated deeply for many researchers. Despite of a great number of catalysts for methane and VOCs combustion there is still a need for searching the catalysts which can be applied in structured reactors with sophisticated shapes. The question arises, how to optimize and improve the preparation methods to obtain high catalytic activity of manufactured catalysts and avoid coating shrinkage and cracking during the thermal treatment of coatings placed on structured reactors. Here, we present the catalyst for methane and VOCs combustion based on the thin zirconium dioxide coating doped with non-noble metals prepared by using sonochemical sol-gel method. The preparation method of metal oxide layers on metallic structures was based on the synergistic combination of three approaches: the application of ultrasonic irradiation during the synthesis of Zr sol-gel based on precursor solution containing zirconium(IV) n-propoxide, addition of stabilizing agents and ZrO<sub>2</sub> deposition on the metallic structures by dip-coating method. As a result, the uniform and dense films of zirconium dioxide were obtained on the FeCrAlloy supports. The structured reactors were characterized by various physicochemical methods such as BET, AFM, EDX, XRF, XRD and in situ Raman spectroscopy. The developed ultrasound assisted sol-gel method has proven to be an efficient way to obtain thin, well adhered zirconium dioxide layers on the structured reactors that can be used for gas exhaust abatement purposes. In the second step the manufactured catalysts were tested in catalytic combustion of methane and VOCs. The catalysts activity was measured using operando DRIFT spectroscopy using Praying Mantis High Temperature Reaction Chamber (Harrick) connected to a MKS Instruments Cirrus II LM118 online quadrupole mass spectrometer in the temperature range of 100 - 450 °C. The Cr-doped catalyst was the most active in tested reactions. The relative activity was about 20% higher than for the reference Pd catalyst. [1] A. Guldhe, P. Singh, F. Ahmad, B. Singh, F. Bux, Biodiesel synthesis from microalgal lipids using tungstated zirconia as a heterogeneous acid catalyst and its comparison with homogeneous acid and enzyme catalysts, *Fuel*. 187 (2017) 180–188. doi:10.1016/j.fuel.2016.09.053. [2] X. Li, A. Kant, Y. He, H. V. Thakkar, M.A. Atanga, F. Rezaei, et al., Light olefins from renewable resources: Selective catalytic dehydration of bioethanol to propylene over zeolite and transition metal oxide catalysts, *Catal. Today*. 276 (2015) 62–77. doi:10.1016/j.cattod.2016.01.038 The Project was financed by the National Science Centre Poland based on the decision No 2015/17/D/ST8/01252 and partly within National Centre for Research and Development No LIDER/204/L-6/14/NCBR/2015

## Raman spectroscopy characterization of cyclic/acyclic molecular rotors

Tomasz Runka<sup>\*A</sup>, Karolina Olszewska<sup>A</sup>, Piotr Fertsch<sup>A</sup>, Andrzej Lapinski<sup>B</sup>, Izabella Jastrzebska<sup>C</sup>, Rosa Santillan<sup>D</sup>, Norberto Farfán<sup>E</sup>

<sup>A</sup>Faculty of Technical Physics, Poznan University of Technology, Piotrowo 3, 60-965 Poznań, Poland; <sup>B</sup>Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17, 60-179 Poznań, Poland; <sup>C</sup>Institute of Chemistry, University of Białystok, Ciołkowskiego 1K, 15-245 Białystok, Poland; <sup>D</sup>Departamento de Química, Centro de Investigación y de Estudios Avanzados del IPN, México D.F. Apdo. Postal 14-740, 07000, México;

<sup>E</sup>Facultad de Química, Departamento de Química Orgánica, Universidad Nacional Autónoma de México, 04510 México D.F., México.

\*tomasz.runka@put.poznan.pl

**ABSTRACT:** In engineering, we meet different kinds of motors and engines of motion powered by steam, electricity, or internal combustion of fuel used in e.g. jets, rockets, or steam engines. However, it is fascinating to see how Nature itself has found a solution to control movement at the molecular level by the conversion of chemical energy into mechanical energy e.g. during ATP hydrolysis in myosin. This molecular motion of myosin is responsible for the lengthening and shortening of filaments that are intensified and changed into useful macroscale motion. Recently, many efforts are made toward obtaining molecular and supramolecular systems in which changes in shape, switching processes, or movements occur in response to external chemical, electrochemical, or photochemical stimuli. Such systems include the group of molecules containing rotating parts often referred to as molecular rotors. In molecular rotors, part with the smaller moment of inertia about the axle is called rotator and the part with the larger moment of inertia is called stator. In this paper, we present the synthesis conditions and Raman spectroscopy characterization of molecular rotors consisting of steroidal derivatives as stators and 1,4-diethynylphenylene as rotators. Hecogenin acetate was subjected to Grignard ethynylation followed by Sonogashira coupling with 1,4-diiodobenzene- $d_4$ . The obtained acyclic dimer was further transformed into the corresponding 3-ester with the terminal double bond. This compound was converted into the final product (E and Z isomers) via a RCM protocol. The compounds named by us 1 and 2 were prepared for spectroscopic measurements. The Raman spectra were recorded in the spectral range 100 - 3200  $\text{cm}^{-1}$  using as an excitation source He-Ne laser operating at 632.8 nm and near infrared laser operating at 785 nm. On the basis of Raman spectra registered at room temperature for both investigated compounds, the assignment of modes was proposed. In the spectral range 400 - 1500  $\text{cm}^{-1}$  large number of weak bands is observed. The bands in this range can be mainly assigned to vibrations of C–O, C–C, C–H bonds and especially to skeleton vibrations. Above 1500  $\text{cm}^{-1}$  two most intense bands in Raman spectrum were observed at about 1575 and 2215  $\text{cm}^{-1}$  and were attributed to the vibrations of double and triple carbon-carbon bonds, respectively. Weak bands recorded in the spectral range 2850 – 3000  $\text{cm}^{-1}$  were assigned to symmetric and antisymmetric stretching vibrations of C–H bonds. To investigate molecular dynamics of rotors with temperature two above mentioned bands were selected for analysis. Different behaviour with temperature of bands at around 1575 and 2215  $\text{cm}^{-1}$  for 1 and 2 compounds was observed. The appearance of new features with decreasing temperature in two above mentioned bands was observed only for 2. This is due to the presence of non-equivalent double and triple carbon-carbon bonds.



*Speciation Session*  
***Speciation***

(Wed. 14<sup>th</sup> of June, h. 9.15-10.30)

## Spectrometric tools for selenium speciation: oxidation states, metabolites, proteins and nanoparticles

Joanna Szpunar

Institute of Analytical Sciences and Physical Chemistry for Environment and Materials, IPREM, CNRS UMR  
5254, Hélioparc, 2, av. Pr. Angot, 64053 Pau, France

\*joanna.szpunar@univ-pau.fr

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*ABSTRACT: Distinguishing between different selenium chemical forms present in biological systems presents a particular challenge for analytical chemists because of the complex speciation and very narrow selenium essentiality range. Besides having several possible oxidation states in its inorganic form, selenium can be incorporated into tens of known (and probably many more not discovered yet) low molecular weight (less than 1000 Da) selenometabolites, many SeCys- and SeMet-containing proteins, selenosugars, selenolipids and, the last but not least, present as selenium nanoparticles. Each of these forms has a distinct biological function and as such should be individually detected and determined in the presence of a rich biological matrix. Reliable analytical methods for selenium speciation are of utmost importance for life sciences including biochemistry, metabolic and toxicological studies and food sciences. The presentation will discuss state-of-the-art analytical approaches to selenium speciation based on a synergic use of elemental (ICP MS) and molecular (ESI MS<sup>n</sup>) mass spectrometric (MS) techniques. This concept, combining the virtues of both mass spectrometric methods, requires a compromise concerning the separation conditions prior to the MS which have to be applicable to both techniques. The robustness of ICP MS ensures reliable quantitative control of the stability of the species throughout the analytical procedure whereas the recent developments in ESI Orbitrap MS, including resolution of more than 500 000 and sub-ppm mass accuracy together with multistage fragmentation capacity, provide means of reliable identification of unknown, and confirmation of the presence of known, compounds. The speciation information on selenium incorporation into biota is completed by Single-Particle (SP) investigation of the size and number concentration of selenium nanoparticles naturally formed in the metabolic processes. Several applications of the developed analytical approaches to speciation analysis in plants, microorganisms and cultured cell lines will be given.*

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## Probing for metal-ligand interactions and analysis for non-covalent metal complexes in bacteria and plants using chromatography with dual ICP MS and electrospray FT MS detection

Laurent Ouerdane, Ryszard Lobinski

Institute of Analytical Sciences and Physical Chemistry for Environment and Materials, IPREM, CNRS UMR 5254, Hélioparc, 2, av. Pr. Angot, 64053 Pau, France

\*[ryszard.lobinski@univ-pau.fr](mailto:ryszard.lobinski@univ-pau.fr)

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**ABSTRACT:** *Metals are required in many life processes, and consequently all organisms have developed mechanisms for their uptake and homeostasis. Bacteria developed strategies for metal acquisition in metal-deprived environments involving the synthesis of siderophores, their extracellular release prior to capture and import of the siderophore-metal, typically  $\text{Fe}^{3+}$ , complex. In plants, metal species play an essential role in maintaining the structure and the enzymatic activity of cells. Plants have evolved their own metal chelators and among them, nicotianamine is an important metabolite that is essential in the homeostasis of iron, copper, nickel and zinc. An excess of certain metals can lead to severe toxicity because of metal substitutions in enzymes and oxidative damage. For the above reasons, it is crucial to determine the nature of metal species to better comprehend their fate and their role in organisms. Generally associated with organic molecules, metals are usually present in low concentrations (nM to  $\mu\text{M}$  ranges) and occur distributed in a plethora of chemical forms with various properties (covalent or non-covalent species and a wide range of molecular weights). These species are often unstable (labile and prone to oxidation), which makes the analysis cumbersome. Whereas covalent species can be approached by canonical metabolomic procedures, the identification of non-covalent metal complexes at basal concentrations remains a challenge. In particular, de novo identification of previously unreported species and detection of minor species are therefore difficult to achieve. The lecture discusses the developments of analytical methodologies for the probing of the metal complexes in bacterial and plant ligand environment, the identification of the species present and their quantitative determination. The procedures involved hydrophilic interaction chromatography with dual detection by elemental (inductively coupled plasma mass spectrometry) and molecular (high-resolution electrospray mass spectrometry) mass spectrometric detection. In terms of applications two case studies will be discussed: (i) exploratory strategies for the discovery and characterization of a new bacterial siderophore, staphylopin, and (ii) large-scale (> 10 metals, > 50 metal complexes) detection, identification and semi-quantitative determination of metal complexes in the xylem and embryo sac liquid of the green pea, *Pisum sativum*. The methodologies developed provide a large inventory of various types of metal complexes, which is a significant asset for future biochemical and genetic studies into metal transport/homeostasis.*

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## Direct Speciation Analysis of Arsenic in Whole Blood and Blood Plasma at Low Exposure Levels by Hydride Generation-Cryotrapping-ICP-MS: A New Trick of an Old Dog.

Tomáš Matoušek<sup>\*A</sup>, Zhifeng Wang<sup>B,C</sup>, Christelle Douillet<sup>B</sup>, Stanislav Musil<sup>A</sup>, Miroslav Stýblo<sup>B</sup>

<sup>A</sup>Department of Trace Element Analysis, Institute of Analytical Chemistry of the CAS, Brno, Czech Republic.

<sup>B</sup>Department of Nutrition, Gillings School of Global Public Health, University of North Carolina at Chapel Hill, Chapel Hill, USA. <sup>C</sup>School of Environmental Science & Engineering, Shandong University, Jinan, China.

\* matousek@biomed.cas.cz

**ABSTRACT:** Arsenic is a toxic element present in body fluids in number of species. From the point of arsenic toxicokinetics and metabolism, the most interesting species found in blood are inorganic arsenic (iAs, as a sum of arsenite, iAs<sup>III</sup> and arsenate, iAs<sup>V</sup>) and their methyl derivatives, mono- (MAs) and dimethylated arsenic (DMAs), also in tri- and pentavalent forms. Compared to commonly analyzed urine samples, speciation analysis of arsenic in whole blood and blood plasma is no easy task. The typical arsenic concentrations in unexposed blood are in low  $\mu\text{g l}^{-1}$  or below, which is right at or beyond the limits of the workhorse method of speciation analysis, HPLC-ICP-MS. A well-known technique of selective hydride generation with cryotrapping (HG-CT) was developed already in the early 70's. But even nowadays it is an excellent complement of currently used HPLC-ICP-MS methods, which it surpasses especially in sensitivity and in the minimum sample pretreatment needed. Hyphenation to ICP-MS provides ultrasensitive detection. On the other hand, although this method can provide the quantitation of the most toxicologically interesting species, it cannot provide complete arsenic speciation. A method for analysis of toxicologically important arsenic species in blood plasma and whole blood will be presented. The method is a modification of the technique that has been previously validated for number of complex biological matrices including tissue homogenate. Preparation of blood or plasma samples involves only 5 times dilution with addition of Triton X-100, Antifoam B and L-cysteine for prereduction of As species. This combination of surfactants suppresses excessive mixture foaming in the hydride generator. Slopes of calibration graphs measured in samples of whole blood and blood plasma spiked with iAs, MAs and DMAs at 0.25-1  $\mu\text{g l}^{-1}$  As levels for HG-CT with AAS detection and at 0.025- 0.1  $\mu\text{g l}^{-1}$  As levels with ICP-MS detection did not differ from slopes obtained from aqueous solutions. Samples with elevated arsenic content in form of species generated in the process of As metabolism- plasma from leukemia patients treated by arsenic trioxide and whole blood from mice fed arsenic containing diet- were analyzed after mild phosphoric acid digestion and results were in a good agreement with results of direct analyses by HG-CT AAS. These plasma samples containing naturally occurring arsenic metabolites were then used as a spiking material to plasma and blood matrix, at sub  $\mu\text{g l}^{-1}$  levels, corresponding to low arsenic exposure. HG-CT-ICP-MS analysis provided for all species recoveries of 88-104% from blood plasma and 91-99% from whole blood. The precision of measurements in plasma and whole blood samples was better than 5% and typically better than 3% in the range 0.01 -0.1  $\mu\text{g l}^{-1}$ . Limits of detection in original blood and plasma samples were assessed as 0.003  $\mu\text{g l}^{-1}$  As for iAs and below 0.001  $\mu\text{g l}^{-1}$  As for methylated species. Thus, this method is well suited for analyses of blood plasma and whole blood from individuals at low exposure levels. This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic Kontakt II program project no. LH 15174 and the AS CR institutional support RVO: 68081715.

## Speciation of inorganic selenium in environmental samples after suspended dispersive solid phase microextraction combined with inductively coupled plasma spectrometric determination

Luthando Nyaba\*, Philiswa N. Nomngongo

Department of Applied Chemistry, University of Johannesburg, Doornfontein Campus, P.O. Box 17011, Johannesburg, 2028, South Africa.

\*luther.nyaba@gmail.com

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**ABSTRACT:** A rapid and effective suspended dispersive solid phase microextraction (SDSPME) was developed for the speciation of inorganic selenium using alumina nanoparticles functionalized with Aliquat-336. The target analytes were preconcentrated and determined by inductively coupled plasma optical emission spectrometry. Alumina nanoparticles were characterised using XRD, BET, SEM and EDX while the functionalized nano-Al<sub>2</sub>O<sub>3</sub> was characterized by FTIR. The effect of pH of the solution on speciation Se in water samples was optimized separately. It was observed that when the pH values of sample solution ranged from 2.0-7.0, successful separation of inorganic Se species was achieved. The percentage recoveries for Se (IV) and Se (VI) were > 90% and 5%, respectively. The two-level fractional factorial design was used to optimize experimental parameters affecting the preconcentration system. Under optimal conditions, the enrichment factor (EF), limit of detection (LOD) and limit of quantification for Se (IV) were found to be 850, 1.4 ng L<sup>-1</sup>, and 4.6 ng L<sup>-1</sup>, respectively. Furthermore, intra-day and inter-day precisions expressed in terms of relative standard deviation (RSD) were found to be 1.9 and 3.3%, respectively. The effect of coexisting ions on the recovery of Se (IV) was investigated. The accuracy of the developed method was checked by analysis of standard reference material (NIST SRM 1643e). The optimised method was applied for the determination of targets in surface water samples.

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## Speciation Analysis of Arsenic Compounds in Marine Samples

Agnieszka Nawrocka, Maciej Durkalec, Mirosława Kmiecik and Andrzej Posyniak

Department of Pharmacology and Toxicology,  
National Veterinary Research Institute Al. Partyzantów 57, Puławy, Poland

\*agnieszka.nawrocka@piwet.pulawy.pl

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*Arsenic (As) is non-essential and one of the most toxic component of the Earth's crust. An environmental transport of this element as a result of natural and anthropogenic processes, causes its bioaccumulation in the food chain. Arsenic occurs in different chemical forms, differing in the bioavailability and toxicity. Inorganic arsenic (As (III), As (V)) and its organic metabolites (MMA, DMA) characterizes the highest toxicity, therefore the control of their levels in food of animal origin is an important element in the human's health protection. Aquatic organisms, due to their sedentary or sessile lifestyle, are particularly exposed to arsenic through waterborne and dietary routes. The aim of this study was to assess the concentration levels of six arsenic species: arsenite As(III), arsenate As(V), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenobetaine (AsB), and arsenocholine (AsC)). Determination of six arsenic forms was carried out by high performance liquid chromatography combined with inductively coupled plasma mass spectrometry (HPLC-ICP-MS) with one anion exchange column. The solvent extraction method, using mixture of methanol/water was used for releasing arsenic species in analysed samples. Extraction efficiency was confirmed by determination of total arsenic in obtained extracts via ICP-MS. Speciation analysis was performed in bivalve molluscs available on the Polish market: dog cockle (*Glycymeris glycymeris*), Manila clam (*Ruditapes philippinarum*), Atlantic jackknife clam (*Ensis directus*), blue mussel (*Mytilus edulis*), Pacific oyster (*Crassostrea gigas*), great scallop (*Pecten maximus*), common cockle (*Cardium edule*) and hard clam (*Mercenaria mercenaria*). Samples originating from five countries were collected on local warehouses and markets according to the multi-annual monitoring programme "Protection of animal and public health". The major arsenic species in bivalve molluscs was arsenobetaine, non-toxic chemical form of arsenic. Inorganic arsenic was generally not detected in most samples. Reliability of results obtained was verified by analysis of spiked samples, certified reference materials (CRMs) and participation in the international proficiency testing. The research was supported by KNOW (Leading National Research Centre) Scientific Consortium "Healthy Animal - Safe Food", decision of Ministry of Science and Higher Education No. 05-1/KNOW2/2015.*

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*Atomic Spectrometry Session*  
***Atom Spect***

(Wed. 14<sup>th</sup> of June, h. 11.00-13.35)



## The role of charge transfer in matrix-induced non-spectral interferences in inductively coupled plasma atomic emission and mass spectrometry.

Margaretha de Loos-Vollebregt<sup>\*A</sup>, Guillermo Grindlay<sup>B</sup>, Raquel Serrano<sup>B</sup>, Juan Mora<sup>B</sup>

<sup>A</sup>Ghent University, Department of Analytical Chemistry, Krijgslaan 281 – S12, 9000 Ghent, Belgium; <sup>B</sup>University of Alicante, Department of Analytical Chemistry, Nutrition and Food Sciences, PO Box 99, 03080 Alicante, Spain.

\*margaretha.delooos@ugent.be

**ABSTRACT:** In inductively coupled plasma atomic emission and mass spectrometry, the signal of some hard-to-ionize elements is selectively enhanced by the presence of carbon, sulfur or phosphorus. This effect has been explained by increased ionization due to a charge transfer reaction between the concomitant ions and analyte atoms, followed by an ion-electron recombination process [1-4]. This results in an increased population of ions as well as excited analyte atoms in the plasma [1-4]. ICP-MS results show that P, As, Se, Sb, Te, I, Au and Hg sensitivities are higher for carbon-containing solutions than those obtained without carbon, whereas P, As, Se and Te are also enhanced in the presence of sulfuric acid. The atomic emission intensities of As, Se and Te are enhanced by a carbon-, sulfur- or phosphorus-containing matrix. Iodine and P emission are enhanced in the presence of carbon and sulfur, whereas Hg emission is only enhanced in the presence of carbon. Signal enhancement is more significant for those electronic transitions involving the highest upper energy levels. The influence of charge transfer reactions depends on experimental conditions. The use of a robust plasma (i.e. using high r.f. power and lower nebulizer gas flow rates) improves carbon, sulfur and phosphorus ionization in the plasma and, hence, signal enhancement due to charge transfer is more pronounced. Due to the presence of easily ionizable elements the ionization is somewhat reduced and consequently signal enhancement due to charge transfer becomes less pronounced. Although the matrix effects are to some extent explained by changes in the plasma characteristics and differences in ion distribution in the plasma, it has been demonstrated that they are also related to charge transfer reactions involving charged species of concomitant ions in the plasma. The occurrence of charge transfer reactions may influence the accuracy of the analytical method. However, the charge transfer process can also be used to improve the limits of detection for the affected elements. To take advantage of this effect, better knowledge of its fundamentals is mandatory. Literature on this topic will be comprehensively discussed to highlight the role of charge transfer reactions in ICP-AES and ICP-MS analysis.

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## New Findings on the Direct Analysis of Solid Samples Using Atomic and Inorganic Mass Spectrometry

Daniel L. G. Borges<sup>\*A</sup>, Jefferson S. de Gois<sup>A,B</sup>, Tarcísio Silva de Almeida<sup>A</sup>

<sup>A</sup>CFM-Chemistry Department, Federal University of Santa Catarina, Florianópolis-SC, Brazil; <sup>B</sup>Chemistry Institute – Department of Analytical Chemistry, Rio de Janeiro State University, Rio de Janeiro-RJ, Brazil.

\*daniel.borges@ufsc.br

**ABSTRACT:** Despite the significant advances, sample preparation remains as a critical step of any analytical method. Hence, the idea of directly analyzing solid samples has always been appealing as direct analytical methods are associated to characteristics such as reduced risk of contamination and/or analyte loss, increased detection power due to the absence of dilution and typically higher sample throughput when compared to 'wet chemistry' methods. Our research group has been devoted to the systematic development of methods that include the direct insertion of solid samples into a graphite furnace, as a means to quantify trace elements using high-resolution continuum source atomic absorption spectrometry (HR-CSAAS) and inductively coupled plasma mass spectrometry (ICP-MS). Analytical methods employing HR-CSAAS involved positioning especially-designed L'vov platforms containing a previously weighed aliquot (typically 0.05-1 mg) of a solid sample into a graphite furnace. Several methods were developed, which include the simultaneous determination of Cr, Co and Ni in carbon nanotubes using calibration approaches that involved the integration of analytical signals at line wings, hence, expanding the linear calibration range to high concentrations. Similarly, atmospheric particulate matter samples were analyzed for their Be, Cd, Cr, Pb, Co, Fe and Ni content, the latter three being determined simultaneously. Parameters such as the background absorption due to the fine rotational spectra of molecules as SiO and PO have been investigated and accurate results were obtained, with LODs that ranged from 0.001 to 0.3  $\mu\text{g g}^{-1}$ . Direct analysis of stimulant plants has also been investigated aiming at Mn, Ni, Rb and Sr determination in addition to the establishment of their polyphenol content and antioxidant activities. Specific species of plants could be fully discriminated with the aid of principal component analysis. Quantitative analysis of halogens using electrothermal vaporization ICP-MS has also been accomplished using direct analysis with the 'cup-in-tube' technique. Coal, biological materials and atmospheric particulate matter samples have been analyzed directly often using calibration against aqueous standards. Pre-dried modifiers such as Pd and/or Ca allowed the analytes to remain thermally stable and several parameters, such as aerosol carriers, pyrolysis and vaporization temperatures and operating parameters have been investigated and optimized. Applications include the quantification of Cl in biological materials, Cl and Br in coal and the halogen profiling (F, Cl, Br and I) of atmospheric particulate matter, with typical LOD at sub  $\text{mg g}^{-1}$  for Cl and sub  $\mu\text{g g}^{-1}$  for Br and I. Overall, the range of application examples that were developed in our research group allow to conclude that direct solid analysis is, indeed, a feasible and time-saving approach, which adds simplicity to the task of determining trace metals and non-metals in a wide variety of samples.

## Development of a Battery-Operated, Portable Atomic Emission Analyzer for Elemental Analysis Based on Atmospheric Pressure Glow Discharge Excitation Source

Zhenli Zhu<sup>\*A</sup>, Chun Yang<sup>A</sup>, Dong He<sup>A</sup>, Hongtao Zheng<sup>A</sup>

<sup>A</sup>State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan, China.

\*zlzhu@cug.edu.cn

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**ABSTRACT:** In this study, a sensitive atomic emission spectrometer (AES) based on a new low power and low argon consumption ( $< 10\text{ W}$ ,  $100\text{ mL/min}$ ) miniature direct current (DC) atmospheric pressure glow discharge (APGD) plasma ( $3\text{ mm} \times 5\text{ mm}$ ) excitation source was developed for elemental determination in water samples. In this method, heavy metals in water was reduced to their hydride form by hydride generation (HG), which was then transported to the APGD source for excitation and detected by a compact CCD (charge-coupled device) microspectrometer. Different parameters affecting the APGD and the hydride generation reactions were investigated. The detection limit for As, Hg, Cd and Pb with the proposed APGD-AES were all below  $1\text{ }\mu\text{g/L}$ , and the calibration curves were found to be linear up to 2 orders of magnitude. It was also demonstrated that the sensitivity of the proposed APGD-AES could be significantly enhanced by gas flow-interruption. In that mode, the LODs could be improved at least one order of magnitude for As and Sb. The proposed method was successfully applied to the determination of certified reference material (GBW08605), tap water, pond water, groundwater and hot spring samples. Measurements from the APGD analyzer showed good agreement with the certified value/values obtained with well-established hydride generation atomic fluorescence spectrometry (HG-AFS). These results suggest that the developed robust, cost-effective, and fast analyzer can be used for field based elemental determination and may provide an important tool for heavy metal contamination and remediation programs.

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## **Removing interferences with the MS-MS technology in triple quadrupole ICP-MS to improve the analytical detection of inorganic nanomaterials.**

Paolo Scardina<sup>A</sup>

<sup>A</sup>Agilent Technologies Italia S.p.A. via Gobetti 2/c Cernusco sul Naviglio – Milano

paolo.scardina@agilent.com

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*ABSTRACT: ICP-MS is the most powerful technique for the determination of trace elements and, operated in single particle mode or hyphenated to fractionation techniques (e.g. Field Flow Fractionation), is widely used for detecting inorganic nanoparticles. Agilent has developed a second generation of QQQ-ICP-MS systems able to increase the power of interferences removal and decrease the background for elements, such as silicon (Si), titanium (Ti) and iron (Fe), which are used as analytical masses in the determination of nanomaterials of importance in the agri-food sector. The presentation focuses on the reaction strategy used in ICP-MS/MS to remove the above-mentioned polyatomic interferences.*

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## Quantitative depth profile analysis of rare earth elements in corroded steel by glow discharge - time of flight mass spectrometry

Rocío Muñiz<sup>\*A</sup>, Lara Lobo<sup>A</sup>, Timothy Kerry<sup>B</sup>, Clint Sharrad<sup>B</sup>, Rosario Pereiro<sup>A</sup>

<sup>A</sup> Department of Physical and Analytical Chemistry, Faculty of Chemistry, University of Oviedo. C/Julian Claveria 8, 33006, Oviedo, Spain. <sup>B</sup> School of Chemical Engineering and Analytical Sciences, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK.

\*rociomunizdelgado@gmail.com

**ABSTRACT:** One of the primary materials used in facilities that handle and manipulate nuclear fuel is stainless steel. However, it has previously been shown that this material can become contaminated and pose a costly liability to the industry. Through a tailored decontamination procedure the material may be disposed of more cheaply or even reused or recycled. Whilst previous research has focused on short term contamination experiments of hours or days there is little understanding of contaminant behaviour over longer time periods. Moreover, limited work has investigated penetration of contaminants at depth, an issue which could complicate decontamination efforts. In this line, studies have been carried out on corrosion and contamination of stainless steels with inactive rare earth element substitutes to radioactive materials. Pulsed glow discharge (PGD) coupled to time of flight mass spectrometry (TOFMS) allows sensitive elemental depth profiling with nanometric resolution of almost all elements of the periodic table. Therefore, PGD-TOFMS appears to be an interesting and innovative tool to study the depth profile of these contaminants after corrosion under different experimental conditions: e.g. varying the acidity of the medium, the surface finishes and the time period in which surfaces are exposed to contaminants.

- **Methods:** The recently commercialized instrument by HORIBA "PP-TOFMS, Plasma Profiling Spectrometer" has been here investigated in the analysis of stainless steel substrates contaminated with different rare earth elements (Ce, Eu, Nd and Sm) as inactive substitutes to radioactive materials. After optimization, PGD-TOFMS operating conditions selected were 40 W of GD applied power, 160 Pa of pressure inside the discharge chamber and 1ms GD pulse with a pulse period of 4 ms. The effect of blanking was also investigated to increase sensitivity. Here, it should be noted that blanking is an interesting feature of this new instrument, as it has a quadrupole that can act as a filter of ions previous to the TOFMS, to avoid overloading of the detector.

- **Results:** Results confirmed that if we blank  $^{40}\text{Ar}^+$  (discharge gas) and  $^{56}\text{Fe}^+$  (matrix element), the detection sensitivity of the analytes increases noticeably. Next, we developed a strategy of quantification as there were no suitable CRMs available containing all the elements of interest. Quantitative depth profiles of four samples have shown that the contaminant didn't penetrate the substrate more than 100 nm in the month they were exposed to, being this an interesting novel finding.

- **Conclusions:** The work carried out demonstrates the capabilities of the novel PP-TOFMS instrument for depth profiling and that the use of blanking improves the sensitivity of the analytes in these samples. Also, the strategy of quantification proposed has allowed solving the problem of quantification since the results of validation were consistent with the certified concentrations.

## Ligandless Extraction of Trace Amount of Lead Ion by Solidified Floating Organic Drop Microextraction and Determination by Atomic Absorption Spectrometer

Ilknur Durukan Temuge<sup>\*A</sup>, Çiğdem Arpa Şahin<sup>B</sup>, Sema Bektaş<sup>B</sup>

<sup>A</sup>Department of Environmental Engineering, University of Hacettepe, Ankara, Turkey; <sup>B</sup>Department of Chemistry, University of Hacettepe, Ankara, Turkey.

\*ilknurt@hacettepe.edu.tr

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**ABSTRACT:** Trace amount of lead ion in environmental samples was determined by solidified floating organic drop microextraction for preconcentration prior to flame atomization atomic absorption spectrometry. By the help of the proposed method, lead analysis in environmental samples is possible in an ordinary flame atomic absorption spectrometry even at trace levels. The lead ion formed hydrophobic complex by anionic surface active agent sodium dodecylbenzenesulfonate (SDBS) and potassium iodide (KI) that was extracted using a drop of 1-dodecanol. All significant parameters affecting the analytical performance were studied. Optimum pH value was found as 3.5. Optimum sample volume, SDBS concentration, KI concentration and extraction solvent volume were found as 75 mL, 50 mM in dodecanol, 0.02 M and 75  $\mu$ L, respectively. In addition, optimum extraction time was obtained as 30 min, optimum extraction temperature was 45 °C, optimum stirring rate was 650 rpm and ideal extraction phase volume was 0.50 mL, respectively. Methanol was quite effective to use as diluent. Under the optimum conditions, the enhancement factor was 73, the limit of detection (3s) and precision were 3.3 ng/mL and 1.03% ( $n = 9$ , 100 ng/mL), the limit of quantification (10 s) was 10 ng/mL and linear working range was 15-100 ng/mL, respectively. The accuracy of the developed method was evaluated by analyzing a certified reference material. The optimized method was employed for the determination of Pb(II) in environmental samples.

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## AtomAnalyzer: new dimension in spectral data analysis

Jakub Klus\*<sup>A</sup>, Ondřej Beňuš<sup>A</sup>, Jan Novotný<sup>A</sup>, David Procházka<sup>A</sup>, Pavel Pořízka<sup>A</sup>, Jozef Kaiser<sup>A</sup>

<sup>A</sup>AtomTrace a.s. Kolejní 9, 612 00 Brno, Czech Republic

\* info@atomtrace.com

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*ABSTRACT: Newly developed software, AtomAnalyzer, its features and benefits will be presented. New approach in data processing will be shown with emphasis on user-friendly interface and intuitive control. The main advantage is creating the data processing algorithm itself, there is no need to write any code or to be overwhelmed by tables with partial results. The so-to-say story of your data analysis will lead you through graphical interface, leaving no space for confusion. It also enables the possibility to share and supervise easily each others works. It is applicable to any necessary data analysis (qualitative and quantitative, classification, mapping and depth profiling). It contains optimized database of most common spectral lines detectable in LIBS spectrum. The software AtomAnalyzer was originally designed for LIBS purposes but is naturally applicable also to other techniques, which deals with spectra processing, such as LA-ICP-OES/MS, Raman spectroscopy, etc.*

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# *Proteomics Session*

## ***Proteomics***

(Wed. 14<sup>th</sup> of June, h. 9.15-10.45)

## Electrochemical, site-specific peptide bond cleavage as a novel approach in protein analysis

Tao Zhang<sup>A</sup>, Floris T. G. van den Brink<sup>B</sup>, Mathieu Odijk<sup>B</sup>, Hjalmar P. Permentier<sup>A</sup>,  
and Rainer Bischoff<sup>\*A</sup>

<sup>A</sup>Department of Analytical Biochemistry, Groningen Research Institute of Pharmacy, University of Groningen, Antonius Deusinglaan 1, 9713 AV Groningen, the Netherlands; <sup>B</sup>BIOS–Lab on a Chip Group, MESA+ Institute for Nanotechnology and MIRA Institute for Biomedical Technology and Technical Medicine, University of Twente, 7500 AE Enschede, the Netherlands

\*r.p.h.bischoff@rug.nl

**ABSTRACT:** Mass spectrometry-based proteomics plays a central role in protein identification and quantification in complex biological matrixes starting with protein digestion followed by analysis of the resulting peptides by reversed-phase liquid chromatography coupled to tandem mass spectrometry. Enzymatic digestion with proteases is the most widespread method for cleavage of proteins at specific peptide bonds, and a number of proteases with different specificities are available. Chemical cleavage is sometimes used as an alternative to enzymatic digestion if specificity for a certain amino acid sequence is required for which no protease is known. Electrochemical oxidation of peptides and proteins has been shown to lead to specific cleavage of the peptide bond C-terminal to Tyr and Trp, which makes electrochemistry (EC) a potential instrumental alternative to chemical and enzymatic peptide bond cleavage, since EC is fast, does not require the addition of reagents, and works under denaturing conditions.

Cleavage of the peptide bond following electrochemical oxidation of Tyr or Trp results in a spirolactone moiety at the newly formed C-terminus offering a handle for chemical labeling. Based on these attributes, we developed a highly efficient and selective chemical labeling approach based on spirolactone chemistry. Since electrochemically-generated peptide-spirolactones readily undergo an intramolecular rearrangement yielding isomeric diketopiperazines, we established a procedure to prevent intramolecular arrangement by acetylating the N-terminal amino group prior to electrochemical oxidation. This allowed the selective chemical labeling of the tripeptide LWL and the decapeptide ACTH 1-10 with amine-containing reagents to introduce a fluorescent label or biotin for detection or affinity enrichment. Subsequent work showed that the acetylation step can be avoided when stabilizing the spirolactone against intramolecular rearrangement by including  $\text{Cu}^{2+}$  in the reaction mixture.

Initial experiments with transferring these reactions to a microfluidic chip with an integrated boron-doped diamond electrode show proof-of-principle of an electrochemical device for site-specific protein digestion. Electrochemical digestion of peptides and proteins followed by chemical labeling may constitute a new, powerful tool in protein chemistry and protein analysis

We gratefully acknowledge the Dutch Technology Foundation (STW, Project 11957) for the support of this work.

## Metal-Tagging Strategy for Bioanalysis: Quantification of Protein Biomarkers and Counting Cells

Qiuquan Wang<sup>\*A, B</sup>, Yong Liang<sup>A</sup>, Chunlan Liu<sup>A</sup>, Nannan Tang<sup>A</sup>, Limin Yang<sup>A</sup>

<sup>A</sup> Department of Chemistry & the MOE Key Lab of Spectrochemical Analysis and Instrumentation, College of Chemistry & Chemical Engineering, Xiamen University, Xiamen 361005, China; <sup>B</sup> State Key Lab of Marine Environmental Science, Xiamen University, Xiamen 361005, China

\*qqwang@xmu.edu.cn

**ABSTRACT:** Inductively coupled plasma mass spectrometry (ICPMS) is one of the most effective tools for elemental analysis. Recent studies demonstrated that protein biomarkers could be quantified via the determination of the elements, which were chemoselectively and/or biospecifically tagged/labeled on the targeted protein biomarkers, using isotope dilution ICPMS. Furthermore, cells could be easily counted when the targeted biomolecules were membrane proteins. I will talk about some studies performed in my laboratory: how to design and assemble a metal-tag towards a targeted protein biomarker with chemoselectivity and/or biospecificity.<sup>1-2</sup> Click chemistry mediated and metabolism-based metal-tagging/labeling strategies will be focused to talk. Quantification of protein biomarkers and their post tyrosine-phosphorylation and sialic acid-glycosylation as well as counting of their host cells as exemplified will be presented.<sup>3-4</sup> I hope to bring new enlightening ideas to our worldwide colleagues working in the field of ICPMS-based bioanalysis, stimulating them and ourselves to engage more fundamental studies and develop more applications of ICPMS-based bioanalysis.

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## Bioimaging of proteins in biological tissue sections by LA-ICP-MS using bioconjugated gold nanoclusters

María Cruz Alonso<sup>A</sup>, Beatriz Fernández<sup>A,B</sup>, Heike Traub<sup>C</sup>, Lydia Álvarez<sup>B,D</sup>, Héctor González Iglesias<sup>B,D</sup>, Norbert Jakubowski<sup>C</sup>, Rosario Pereiro<sup>\*A,B</sup>

<sup>A</sup>Department of Physical and Analytical Chemistry, University Of Oviedo, C/Julian Clavería 8, Oviedo, Spain; <sup>B</sup>Instituto Universitario Fernández-Vega, Fundación de Investigación Oftalmológica, University of Oviedo, Spain; <sup>C</sup>Bundesanstalt für Materialforschung und -prüfung (BAM), Richard-Willstaetter-Strasse 11, 12489 Berlin, Germany; <sup>D</sup>Instituto Oftalmológico Fernández-Vega, Avda. Dres. Fernández-Vega, 34, 33012 Oviedo, Spain.

\*mrpereiro@uniovi.es

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**ABSTRACT:** Laser ablation (LA) coupled to ICP-MS has shown interesting capabilities in life sciences for trace element mapping of biological tissues. Moreover, the combination of immunoassays with LA-ICP-MS can facilitate protein bioimaging through proper tagging. For such purpose, the use of metal nanoclusters (NCs) as tags will provide high signal amplification: as compared to polymeric tags, its ratio “number of metal atoms/size” is very high because they do not contain carbon or other nonmetals, resulting in an advantageous sensitive strategy to determine antigen distributions (so, allowing to use very small laser spots). In this context, we bioconjugated AuNCs (our synthesized AuNCs have a particle size of 2.7 nm and 580 atoms per NC) with the corresponding antibody and immunoassays in 5 microns thick tissue sections have been developed. After the immunoassay protocol, detection and imaging was carried out by LA-ICP-MS by measuring the Au signal (observed background was negligible) and results compared by fluorescence confocal microscopy (AuNCs are also fluorescent). The methodology has proved successful for the high resolution bioimaging of Metallothioneins (selected as a proof of concept) in different biological tissues, thus opening the way for the development of high resolution and high sensitive methods based on metal NCs for multiplex protein bioimaging by LA-ICP-MS.

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## Comprehensive quantitative study of Zn and Metallothioneins in eye tissue sections and cultured cells by mass spectrometry-based methodologies

Sara Rodríguez-Menéndez<sup>\*A,B</sup>, Héctor González<sup>B,C</sup>, Beatriz Fernández<sup>A,B</sup>, Montserrat García<sup>B,C</sup>, Lydia Álvarez<sup>B,C</sup>, Miguel Coca-Prados<sup>B,C</sup>, Rosario Pereiro<sup>A,B</sup>

<sup>A</sup>Dept. Physical & Analytical Chemistry, University of Oviedo, Julian Clavería, 8, 33006, Oviedo, Spain; <sup>B</sup>Fundación de Investigación Oftalmológica Fernández Vega, University of Oviedo; <sup>C</sup>Instituto Universitario Fernández Vega, University of Oviedo, Avda. Dres Fernández-Vega, 34, 33012, Oviedo, Spain.

\*rodriguezmenendez.sara@gmail.com

**ABSTRACT:** Aged-Related Macular Degeneration (AMD) is one of the leading causes of irreversible blindness among elder people in developed countries. The main hallmark of this pathology is the buildup of extracellular deposits (drusen) between Bruch's membrane and retinal pigment epithelium (RPE). These deposits can reach millimolar levels of zinc. On the other hand, Metallothioneins (MTs) are the main proteins that serve as zinc-ion sensors, involved in the neuroprotection and defense mechanism against oxidative damage. We previously proposed the Zn-MTs redox cycle as a potential therapeutic target of AMD. [1] Therefore, the development of new methodologies for Zn-MTs quantification and distribution in eye tissues might provide useful information for a better understanding of processes involved in AMD.

- **Methods:** Molecular biology and optical-microscopy based methodologies are not enough to study the role of Zn and MTs in drusen formation. Therefore, the use of complementary tools based on Mass Spectrometry may contribute to the study of this process. In this communication, advanced methodologies based on High-Performance Liquid Chromatography (HPLC) and Laser Ablation (LA) coupled to ICP-MS detection will be presented to study the Zn-MTs system in ocular tissues and cells.

- **Results:** First, a quantitative Zn-bioimaging methodology has been developed to study the concentration and distribution of Zn in human ocular tissues distinguishing retina, sclera, choroids and RPE regions by LA-ICP-MS. We found a preferential distribution of Zn in RPE-choroids followed by retina and sclera; these results have been confirmed by the total quantification of Zn by conventional nebulization ICP-MS. Also, preliminary studies related to new strategies for high spatial resolution bioimaging of Zn in culture cells will be presented. Moreover, we have developed a quantitative speciation methodology by post-column isotopic dilution analysis (IDA)-HPLC-ICP-MS to study the Zn-MTs redox system in human ocular tissues (RPE and retina) and in cultured cells (HRPEsv). Quantitative speciation studies showed that Zn is mostly bound to low and medium molecular mass proteins in retina, whereas in RPE is mainly associated to low molecular mass proteins. Then, stoichiometric changes of Zn-MTs complex were determined in HRPE cells using inductors of MT proteins. Experimental results showed that HRPE cells under induction conditions with exogenous zinc and dexamethasone induced a higher MTs synthesis and stoichiometric changes in MTs.

- **Conclusions:** The integrated analytical approach developed, based on LA-ICP-MS and HPLC-ICP-MS for the study of human ocular tissues and culture cells, sheds light on the role of Zn-MTs in AMD disease and paves the way for searching potential therapeutic targets.

[1] H. González-Iglesias et al. *Metallomics*, 2014, 6, 201-208.

# *Fuels Session*

## ***Fuels***

(Wed. 14<sup>th</sup> of June, h. 9.15-10.40)

## Feasible Sample Preparation Methods for further Rare Earth Elements Determination

Érico Marlon de Moraes Flores\*

Chemistry Department, Federal University of Santa Maria, Campus Universitário, Camobi, Santa Maria-RS, Brazil.

\*ericommf@gmail.com

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*ABSTRACT: Nowadays, there is a need for suitable methods for the determination of rare earth elements (REE) in many matrices. Some analytical techniques have been used for the determination of REE, such as neutron activation analysis (NAA), inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS). Despite some advantages, these techniques can present some drawbacks, as the long time for analysis and the necessity of using a nuclear reactor (in case of NAA), as well as several spectral interferences common for ICP OES. Inductively coupled plasma mass spectrometry can be considered as the most suitable technique for the determination of REE, enabling good sensitivity and multielemental capability. The determination of REE by ICP-MS has been generally performed using nebulization systems, making necessary the use of high efficiency sample preparation methods with low acidity in final digests to minimize interferences. Additionally, it is well known that the digestion of some matrices, as e.g. crude oil, is not a simple task, due to the presence of refractory compounds (resins and asphaltenes, thus making necessary very frequently the use of time-consuming sample preparation methods. In this sense, a suitable digestion efficiency is generally reached if using high amount of acids in closed vessels and high pressure and temperature. However, even considering the recent advances in digestion systems some drawbacks still remain. Taking into account the difficulties involved in REE determination in crude oil, in this lecture modern methods and trends in sample preparation will be discussed as well as the feasibility of using electrothermal vaporization system coupled to ICP-MS for crude oil analysis and REE determination.*

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## ***In situ* spectroscopic studies of methane catalytic combustion over Co, Ce and Pd mixed oxides deposited on a steel surface.**

P. Jodłowski<sup>\*A</sup>, R. J. Jędrzejczyk<sup>B</sup>, D. Chlebda<sup>C</sup>, M. Gierada<sup>A</sup>, J. Łojewska<sup>C</sup>

<sup>A</sup>Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Kraków, Poland; <sup>B</sup>Malopolska Centre of Biotechnology, Gronostajowa 7A, 30-387 Kraków, Poland;

<sup>C</sup>Jagielloian University, Faculty of Chemistry, Ingardena 3, 30-060 Kraków, Poland

\*jodlowski@chemia.pk.edu.pl

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**ABSTRACT:** Methane catalytic combustion is interesting not only from the practical but also from the cognitive point of view, as the mechanism of its oxidation seems still far from being understood. The CH<sub>4</sub> molecule is much chemically resistant which originates from the high Td symmetry and a difficult excitation from the ground <sup>1</sup>A<sub>1</sub> state to triply degenerated <sup>1</sup>T<sub>2</sub> state which is accompanied by its splitting and loss of the original symmetry due to Jahn-Teller effect. In the presence of catalysts, the C-H activation is claimed to proceed through two possible pathways, running either on the metal or metal oxide centers. The first mechanism distinguishes the heterolytic cleavage of C-H bond in methane molecule, which results in the formation of a methyl radical, while the second assumes homolytic breakage by oxygen active species. In this study we deal with the mechanism of methane catalytic combustion over structured catalysts. The aim of this paper was to correlate the information of the catalyst surface intermediates during the methane combustion reaction investigated by in situ DRIFT and catalytic tests. The series of cobalt nanocomposite structured catalysts were obtained by impregnation method from nitrate solutions. Prior to the impregnation step, the kanthal steel carriers were precalcined at high temperature and deposited with the washcoat layer of γ-Al<sub>2</sub>O<sub>3</sub>. The catalyst surface was examined by XRF and in situ μRaman spectroscopy. The methane oxidation over the structured catalyst was tested by in situ DRIFT spectroscopy. The in situ experiments performed under methane oxidative and non-oxidative conditions revealed that formates/carbonates are active intermediates in methane catalytic combustion. The kinetic experiments also revealed that palladium doped cobalt catalyst can be considered as a good alternative for noble-based catalysts used in this study as a reference sample.

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## Determination of metals and metalloids in bioethanol samples using a total sample consumption system coupled to ICP techniques

Carlos Sánchez<sup>\*A</sup>, Charles-Philippe Lienemann<sup>B</sup>, Frank Vanhaecke<sup>C</sup>, José-Luis Todolí<sup>A</sup>

<sup>A</sup> Department of Analytical Chemistry, Nutrition and Food Sciences, University of Alicante, Alicante, Spain; <sup>B</sup> Analysis and Physics division, IFP Energies Nouvelles, Lyon, France; <sup>C</sup> Department of Analytical Chemistry, Ghent University, Ghent, Belgium.

\*carlos.sr@ua.es

**ABSTRACT:** Biofuels are being considered as an effective alternative energy source due to the limited stock of petroleum and the pollution caused by fossil fuels. Bioethanol is one of the most promising renewable energy sources, largely because this fuel can reduce the emission of greenhouse gases by up to 85% when compared to petroleum products. The expanded use of bioethanol has created a need for methodologies for the quality control of this biofuel. The presence of metals and metalloids in bioethanol can cause environmental pollution, health problems and damage in the engines that use it as fuel, even when they are present at very low concentrations only. The origin of these contaminants has not been established clearly and they could be incorporated into the biofuel during the production process or storage, but can also be present in the biomass employed as raw material.

Recently, several analytical methodologies based on ICP-OES and ICP-MS, have been developed and employed successfully for the determination of the metals in ethanol fuel, which is a mixture of bioethanol and gasoline. However, a limited number of studies have focused on the analysis of bioethanol due to the difficulties encountered in carrying out the determination of metals in this kind of samples.<sup>1</sup> Among these difficulties, the most important is the large variety of matrices, containing different organic compounds and variable water contents, thus typically requiring calibration via the method of standard additions.

In the present work, accurate and precise analytical methods based on ICP techniques for the quantification of metals and metalloids in bioethanol samples have been developed. First, fundamental studies using a total sample consumption system, called high-temperature Torch-Integrated Sample Introduction System (hTISIS), have been carried out to remove matrix effects at different ethanol-water ratios. Once the matrix effects for different water contents were overcome, external calibration was applied to quantify major, minor and trace metals present in bioethanol. The methodologies proposed have been validated, obtaining acceptable recoveries and other analytical figures of merit. More than 30 real bioethanol samples of different origin were analyzed. Certain elements such as Ca, K, Mg and Na were found in the order of hundreds of ng g<sup>-1</sup> in most samples studied, whereas for trace analytes as Cr, Cu, Fe, Mg, Ni or Zn, concentrations below 100 ng g<sup>-1</sup> were found in some samples.<sup>2,3</sup>

<sup>1</sup> Metal and metalloid determination in biodiesel and bioethanol, Raquel Sánchez, Carlos Sánchez, Charles-Philippe Lienemann, José-Luis Todolí, J. Anal. At. Spectrom., 30 (2015) 64-101.

<sup>2</sup> Metal and metalloid determination in bioethanol through inductively coupled plasma-optical emission spectroscopy, Carlos Sánchez, Charles Philippe-Lienemann, José-Luis Todolí, Spectrochimica Acta Part B 115 (2016) 16-22.

<sup>3</sup> Analysis of bioethanol samples through Inductively Coupled Plasma Mass Spectrometry with a total sample consumption system, Carlos Sánchez, Charles Philippe Lienemann, José-Luis Todolí, Spectrochimica Acta Part B 124 (2016) 99-108.

## Feasibility of high resolution continuum source flame molecular absorption spectrometry for Si determination in organic solutions via SiO molecule absorption

Zofia Kowalewska<sup>\*A</sup>, Łukasz Gościński<sup>A</sup>, Janusz Pilarczyk<sup>B</sup>

<sup>A</sup> Faculty of Civil Engineering, Mechanics and Petrochemistry, Warsaw University of Technology, Łukasiewicza 17, 09-400 Płock, Poland; <sup>B</sup>Warter Fuels JSC, Chemików 5, 09-411 Płock, Poland

\*zofia.kowalewskah@gmail.com

**ABSTRACT:** High-resolution molecular absorption spectrometry (HR-CS MAS) has been developing fast for determination of non-metals (S, halogens, P, N), but has never been used for Si determination. The element is routinely determined using atomic absorption spectrometry (AAS) and due to refractory character of Si compounds, relatively high atomization temperature is necessary, which is achieved using electrically heated graphite furnace or nitrous oxide - acetylene flame. In this work, for the first time, HR-CS MAS has been applied for silicon determination. The SiO molecule, existing in air-acetylene flame, absorbs radiation in UV range. Intensive rotational lines belonging to various sequences within the electronic transition  $X^1\Sigma^+ \rightarrow A^1\Pi$  were registered in 0.25-0.27 nm intervals (about 20 intervals in the range 216-249 nm). The criteria of choice of the measurement range were: low level of noise, lack of unnecessary signals overlapping SiO molecule spectrum, presence of many high, wide and well separated SiO rotational lines, as well as lack of small, narrow or split SiO lines. To achieve the best sensitivity and detectability, the absorbance of some rotational lines was summed up. The number of pixels taken for signal evaluation and the baseline approximation mode, as well as the flame conditions, were optimized. The application of internal reference was considered. When aspirating xylene solutions, the best characteristic concentration was 0.5 mg L<sup>-1</sup> for SiR (hexamethyldisiloxane) and 2.7 mg L<sup>-1</sup> for SiA (octamethylcyclotetrasiloxane), while the instrumental detection limits were 0.3 mg L<sup>-1</sup> and 1.5 mg L<sup>-1</sup>, respectively. Generally, the noise level for FAAS (nitrous oxide-acetylene flame) was lower than for HR-CS MAS (air-acetylene flame). Comparative analysis of series of organic solutions (fuels, biofuels, dissolved Si organic species) using HR-CS MAS and FAAS showed no statistical significance of the differences of the results obtained using both methods. HR-CS MAS is an attractive alternative to FAAS for Si determination in organic samples at the level of mg L<sup>-1</sup> or higher. Its important advantage is application of ordinary air-acetylene flame, which is less sensitive to the changes of samples composition. Furthermore, the application of HR-CS MAS is much easier, safer and cheaper.

# *Liquid Analysis Session*

## ***Liq. Analysis***

(Wed. 14<sup>th</sup> of June, h. 9.15-10.45)

## Analysis of liquid samples: a great challenge for LIBS

Montserrat Hidalgo\*

Department of Analytical Chemistry and Food Science, and University Institute of Materials, University of Alicante, P.O. Box 99, E-03080, Alicante, Spain.

\*montserrat.hidalgo@ua.es

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*ABSTRACT: Due to the continuous research efforts aimed to improve the analytical performance of LIBS, its use is rapidly expanding into broader applications. The ability of LIBS to perform remote analysis, micro-analysis, depth profiling or spatial chemical mapping allows to obtain analytical information of valuable interest in many different fields, such as geology, art and cultural heritage, terrorism and defence, planetary exploration, etc. These abilities make LIBS special and distinguishable from other, more conventional, instrumental techniques. There is, however, a battery of applications still barely covered by LIBS, particularly those requiring the analysis of liquid samples.*

*Elemental analysis of liquids, of vital importance in a great number of real word applications, has been traditionally performed by well established analytical techniques. In contrast, and mainly due to the comparatively lower quality of the analytical results and to certain experimental limitations, the use of LIBS to this end has been generally hampered.*

*During the latest years, however, the development of early warning analytical systems has become a key issue. The replacement of sophisticated, expensive and slower laboratory instruments with automated and portable analytical system able to perform in situ and real time analysis of liquid samples is, nowadays, of special interests in many situations. Some examples are the need of a continuous water body pollution monitoring, or the importance of a continuous quality control of food or beverages during a manufacturing process.*

*The current scenario of Analytical Chemistry has triggered many researchers to go deeper into the possibilities of LIBS technique to satisfy these emerging demands. To this end, new and innovative analytical strategies for LIBS measurements of liquids are nowadays under study. These include the use of double pulse LIBS, the application of different sample preparation procedures prior to LIBS analysis (i.e., generation of liquid jets or aerosols, conversion of the liquid matrix into a solid, application of extraction procedures, etc.), or the combination of two or several of the mentioned approaches.*

*In this lecture, the difficulties of LIBS analysis of liquids will be presented, and an overview of different procedures aimed to improve its analytical performance will be given. In particular, the talk will mainly be focused on the possibility to hyphenate LIBS detection with modern and easily automatable microextraction methodologies, which can lead to substantial sensitivity improvements in LIBS analysis enabling its use for multielemental detection, at trace levels, in liquid matrices.*

*Acknowledgements:*

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## Study of laser ablation of water droplets with gold nanoparticles

Oscar González Miranda<sup>A</sup>, Tupak García-Fernández<sup>B</sup>, Fausto Bredice<sup>C</sup>, C. Sánchez-Aké<sup>A</sup> and Mayo Villagrán-Muniz<sup>\*A</sup>

<sup>A</sup>Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México, Circuito Exterior S/N, Cd. Universitaria AP 70-186, 04510, Cd. Mx., México; <sup>B</sup> Universidad Autónoma de la Ciudad de México (UACM), Prolongación San Isidro 151, Col. San Lorenzo Tezonco, C.P. 09790, Cd. Mx., Mexico;

<sup>C</sup>Centro de Investigaciones Ópticas, (CIOp), C.C.3, 1897, Gonnet, La Plata, Argentina.

\*mayo.villagran@ccadet.unam.mx

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*ABSTRACT: Optical breakdown in tridistilled water drops, with and without suspended gold nanoparticles on it, was studied by time resolved optical emission spectroscopy, photoacoustic technique and by analyzing the transmittance of the laser pulse energy. For the experiments, the size of the drops was varied. Breakdown was induced by Nd:YAG laser pulses of 10 ns with energy of 100 mJ and duration of 10ns, with two different wavelengths, 532 nm and 1064 nm. In all cases, we found that the presence of nanoparticles reduces the probability of plasma formation. In the particular case of ablation of tridistilled drops without the presence of gold nanoparticles, a decrease in the size of the drops favors the absorption of the laser pulse energy, thus increasing the intensity emitted by the plasma.*

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## Investigating silicon wafer based substrates for ultra-trace determination of metal solutions: Dry droplet analysis by LIBS.

Nadir Aras, Şerife Yalçın\*

İzmir Institute of Technology, Faculty of Science, Chemistry Department, 35430 İzmir, Turkey

\* serifeyalcin@iyte.edu.tr

**ABSTRACT:** Despite to its low detection sensitivity in liquids, Laser Induced Breakdown Spectroscopy still finds a wide-spread use in rapid, in-situ and simultaneous detection of toxic elements in environmental samples. Due to some problems experienced in liquid analysis, much effort has been paid for converting the sample from liquid to solid phase by; freezing into ice, use of adsorbent material, enrichment by electro deposition and drying nano-to-micro droplets on various substrates(1-4). Element and substrate specific enhancements in detection limits up to an order of magnitude have been observed by several groups.

Previously, we have shown detecting sub-picogram amount of copper in nanoliters volume of liquid droplets on silicon oxide coated silicon wafer substrates. Here, we present dry droplet analysis studies on several silicon wafer based substrates to improve the analytical capability of LIBS in liquid droplet analysis. Experiments were performed with a Nd:YAG laser at its second harmonic wavelength and an echelle type spectrograph equipped with an ICCD detector was used. Energetic laser pulses, focused to a relatively large spot outside the minimum focal point condition, were used to form more stable and homogeneous plasma and enhancements in the detection limits were achieved.

Methodology presented is fast and accurate for direct analysis of aqueous samples for environmental monitoring purposes and can also be successfully applied to biological samples where the amount of sample size is limited.

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## Solid phase microextraction (SPME) using carbon-based screen-printed electrodes combined with LIBS technique detection for sensitive elemental analysis.

Francisco Ruiz, Laura Ripoll, Montserrat Hidalgo<sup>\*</sup>, Antonio Canals

<sup>A</sup>Department of Analytical Chemistry, Nutrition and Food Science, University Institute of Materials, University of Alicante, P.O. Box 99, E-03080, Alicante, Spain.

\*montserrat.hidalgo@ua.es

**ABSTRACT:** Portable analytical systems, able to provide in-situ and fast analytical information, are currently in high demand. Clear examples of this are the need of early warning systems for monitoring water quality, in order to prevent for potential human or environmental hazards, or the importance of a continuous quality control in a food or drink industry, for a rapid identification of chemical contaminants in the products. Conventional analytical systems, even if providing high-quality analytical information, are usually voluminous laboratory instruments not useful for field-operation. LIBS systems have much to offer in this regard due to their portability. However, the lack in sensitivity is a limitation for many potential LIBS applications; in special, those involving the monitoring of metal contaminants in liquid samples, which usually have regulatory limits well below the ppm level.

Sample preparation procedures, traditionally tedious and laborious, have advanced considerably in recent years. In particular, there are nowadays miniaturized, fast and efficient extraction methods with possibilities for automation, which can be coupled to LIBS detection to form a fully autonomous, portable and sensitive analytical system. Examples of these new miniaturized extraction methodologies are Solid Phase Microextraction (SPME) processes. In SPME, analytes in the liquid samples are adsorbed and concentrated on a very small quantity of solid sorbent, which can subsequently analysed by LIBS leading to a substantial sensitivity improvement.

When SPME is to be coupled with LIBS, the choice of an adequate solid sorbent is essential. On the one hand, the extraction efficiency of the SPME procedure is highly dependent on the analyte-sorbent affinity and on the solid surface area. On the other hand, as already well known, LIBS emission also depends on the physical and chemical properties of the irradiated solid.

In this work, the influence of the solid sorbent on the coupling of SPME with LIBS detection was investigated. To this end, a SPME procedure termed Thin Film microextraction (TFME) was used. In TFME, the sorbent is coated on the surface of a sheet-like base material, which is then introduced into the liquid sample for extraction of analytes. After extraction, the thin sheet is removed from the solution and dried, in order to perform LIBS analysis of the analyte-enriched sorbent. Commercial carbon-based screen-printed electrodes were used as coated thin films (i.e. mesoporous carbon, graphene oxide, carbon, Au nanoparticles-decorated carbon, Ag nanoparticles-decorated carbon and carbon nanotubes electrodes). Experimental variables affecting the TFME procedure were optimized in order to obtain maximum LIBS emission. Under optimum conditions, analytical figures of merit were evaluated. The obtained results are presented and discussed.

*Acknowledgements:*

*The authors are grateful to the Government of Spain (CTQ2016-79991-R) for the financial support*

## Evaluating the use of Thin Film Microextraction (TFME) with laser-induced breakdown spectroscopy (LIBS) for the detection of trace metals in liquid samples.

Laura Ripoll<sup>A</sup>, Fran Ruiz, <sup>A</sup> Montserrat Hidalgo <sup>A\*</sup>, Antonio Canals <sup>A</sup>, Stefano Legnaioli <sup>B</sup>, Vincenzo Palleschi<sup>B</sup>

<sup>A</sup> Department of Analytical Chemistry, Nutrition and Food Science, University Institute of Materials, University of Alicante, P.O. Box 99, E-03080, Alicante, Spain.

<sup>B</sup> Applied and Laser Spectroscopy Laboratory, Institute of Chemistry of Organometallic Compounds, Research Area of National Research Council, Via G. Moruzzi, 1 – 56124 Pisa, Italy.

\*Montserrat.hidalgo@ua.es

**ABSTRACT:** Solid-phase microextraction (SPME) is an efficient sample preparation strategy for separation and concentration of analytes from a liquid sample. In SPME; a miniaturized version of the traditional Solid Phase Extraction procedure (SPE); analytes in the sample are adsorbed and concentrated on the surface of a small amount of solid material (sorbent). After extraction, and depending on the analytical technique to use, the adsorbed analytes are usually eluted by either a solvent or a thermal desorption process, being finally transported to the instrumental system. Due to its simplicity, SPME appears to be an interesting approach to be combined with LIBS detection for liquid samples analysis. On the one hand, the SPME process results in an analyte-enriched solid matrix to be analyzed by LIBS, which solves the typical experimental problems associated to the analysis of liquid matrices. On the other hand, analytes in the sorbent can be directly analyzed by the LIBS system, therefore avoiding the elution process usually needed when other detection techniques are coupled to SPME.

In this work, a simple and easily automatable modality of SPME, termed Thin Film Microextraction (TFME), was tested as sample preparation procedure for LIBS analysis of aqueous samples. In the proposed TFME-LIBS methodology, glass films coated with a sorbent material were used in the extraction step. The so prepared thin films were introduced into the samples to analyze, which were agitated to assist the extraction process. After extraction, the analyte-enriched films were analyzed by LIBS. Graphene oxide was used as sorbent material, due to its theoretically large surface area available for analyte adsorption. Initial studies were focused on the optimization of the different experimental parameters affecting the TFME procedure, with the aim to maximize both sensitivity and precision in the subsequent LIBS analysis. Under optimum conditions, analytical figures of merit of the TFME-LIBS method were evaluated. Finally, the procedure was applied to the analysis of real aqueous samples. The advantages and limitations of the proposed strategy are presented and discussed.

### Acknowledgements:

The authors are grateful to the Government of Spain (CTQ2016-79991-R) for the financial support. L. Ripoll is grateful to the Ministry of Economy and competitiveness for her PhD fellowship (BES-2012-058759) and for her Mobility grant (EEBB-I-16-I0593).

# *Forensic Applications Session*

## ***Forensic***

(Wed. 14<sup>th</sup> of June, h. 11.00-13.15)

## Fabrication and Falsification in XRF, ICP-AES, HG-AAS and GC-MS in Forensic Analyses in Forensic Analyses in Japan

Jun Kawai

Department of Materials Science and Engineering, Kyoto University, Sakyo-ku, Kyoto, 606-8501, Japan

kawai.jun.3x@kyoto-u.ac.jp

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*ABSTRACT: Spectrochemical analysis methods are used for forensic analyses of murder, arson, and many other criminal cases. I have studied forensic analysis reports of several criminal cases, and among them the arsenic murder case in 1998 and an arson cases in 2013 in Japan have been checked in detail. XRF, ICP-AES, and HG-AAS were used for the arsenic murder case, and GC-MS was used for the arson case. I have found data fabrication in AAS, in such a way that As(III) was reported to be 90 ppb in hair of suspect by HG-AAS, but As(III) is not possible to analyze without changing the chemical state, when the hair was treated by NaOH. Also impurity (Se, Sn, Sb, Pb, Bi) concentration ratios of arsenic samples measured by ICP-AES was multiplied by 1,000,000, and then logarithmic value was plotted in order to show two arsenic evidences were identical. This was equivalent to add 6 to a small number. Thus all the value became quite similar. This is a falsification. XRF was also measured one time for each sample and the statistical deviation was too large to conclude identical, but concluded identical although they were from different origins. GC-MS is quite sensitive for kerosene. However, the detected MS spectrum of strongly burned place was the spectrum of new kerosene composed of small mass components, i.e. low boiling point. This might be due to a contamination from the standard kerosene sample in the laboratory. EPMA, XRD, and LC/MS/MS fabrication or falsification are also reported in other cases.*

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## An integrated multi analytical approach for the investigation of modern inks

Giulia Germinario<sup>A</sup>, Silvia Garrappa<sup>A</sup>, Inez Doroth  van der Werf<sup>A,B</sup>, Antonio Mirabile<sup>C</sup>,  
Luigia Sabbatini<sup>\*A,B</sup>

<sup>A</sup>Dipartimento di Chimica, University of Bari, via Orabona 4, 70125 Bari (Italy); <sup>B</sup>Centro interdipartimentale “Laboratorio di ricerca per la diagnostica dei Beni Culturali”, University of Bari Aldo Moro, Bari (Italy), <sup>C</sup>Paper conservator, 11 rue de Bellefond, Paris (France).

\*luigia.sabbatini@uniba.it

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**ABSTRACT:** Analysis of inks may be important in forensic science, i.e. establishing whether a document is authentic or fraudulent or whether written entries come from a common source (same ink formula). This may require identification of the manufacturer and the specific formula of the ink. Other fields of interest are the investigation of modern art, design and architectural sketches with the purpose of establishing the optimal conservation conditions/treatments or marker pen graffiti where removal could be better accomplished when information on their chemical composition is known. Here, investigation of different classes of modern inks (permanent markers and felt-tip pens) is illustrated. Since inks are complex and heterogeneous systems containing binders, pigments, dyes, solvents, fillers, plasticizers and other types of additives a multi-analytical approach is required. Analyses were performed by means of Fourier Transform Infrared (FT-IR) spectroscopy, Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS), Thin Layer Chromatography (TLC),  $\mu$ -Raman spectroscopy and Surface Enhanced Raman Spectroscopy (SERS). Marker pens of different commercial brands and colors were selected, and felt-tip pens typically used by modern artists were investigated. In particular, Faber Castell felt-tip pens employed by the French modern artist Anne Flore Cabanis, Johann Faber (Presto Color) used by the Brazilian architect Lina Bo Bardi and other artist pens (Stabilo) were studied. The marker pens revealed to contain a wide range of binders comprising not only alkyd, and styrene-acrylic polymers, but also phenolic, ketone and polyvinylacetate resins. In the felt-tip pens styrene-acrylic resins or natural gums were found. The Raman spectra of the marker inks and Faber Castell pens clearly show the presence of phthalocyanine, dioxazine and azo pigments. The Stabilo and Johan Faber inks, instead, contain mixtures of dyes as evidenced by TLC. SERS performed on the TLC spots allowed to identify triarylmethane dyes, rhodamine B and tartrazine, which are characterised by a very low lightfastness index. The evaluation of fading is very important especially when these felt-tip pens are used for the realisation of sketches, artistic and architectural drawings, and technical designs. Here, spectroscopic techniques were also used for the monitoring of photo-accelerated degradation of ink samples.

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## Detection and Mapping of Trace Materials on Surfaces Under Ambient Conditions using Multiphoton Electron Extraction Spectroscopy (MEES) and Comparison to Traditional Spectroscopies

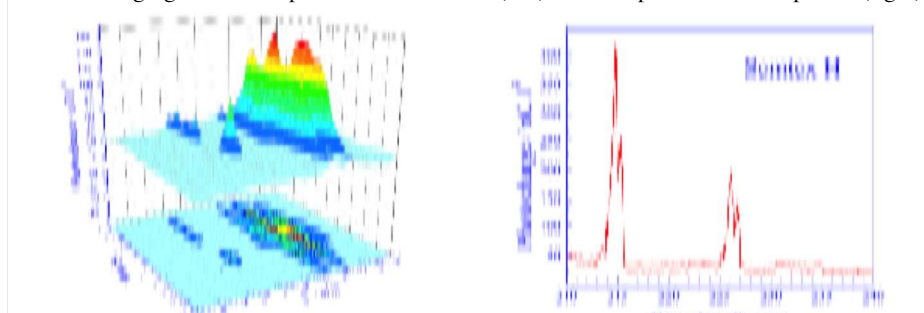
Valery Bulatov, Anneli Kruve, Daniel Fisher, Shisong Tang, Nataly Vinerot, and Israel Schechter\*

Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Haifa 3200, Israel

\*israel@tx.technion.ac.il

**ABSTRACT:** Multiphoton electron extraction spectroscopy (MEES) is a new spectroscopy in which UV laser pulses are utilized for extracting electrons from solid surfaces in multiphoton processes under ambient conditions. Counting the emitted electrons as a function of laser wavelength results in detailed spectral features, which can be used for material identification. MEES has been compared to traditional optical spectroscopies, and the results indicate that its analytical information contents is higher and its sensitivity is comparable to fluorescence (however, it is not limited to fluorescing compounds). The method has been applied to detection of trace compounds on a variety of surfaces. It has been tested for trace explosives, drugs, pesticides, PAHs, and many other materials. The analytical LODs are in the sub pmole range, which indicates that MEES is one of the most sensitive detection methods for solid surface under ambient conditions. Scanning the surface with the laser allows for its imaging, such that explosives (as well as other materials) can be located. The imaging mode is also useful in forensic applications, such as detection of drugs in human fingerprints and in environmental applications such as estimating the coverage of pesticides on plants.

MEES imaging of a swab spiked with Semtex H (left) and the spectrum at a suspected (right)



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## Separation of Overlapping Latent Fingerprint using Laser-Induced Breakdown Spectroscopy Combined with Multivariate Analysis

Jun-Ho Yang and Jack J. Yoh\*

Department of Mechanical and Aerospace Engineering, Seoul National University  
1 Gwanakro, Gwanakgu, Seoul, 151-742 South Korea

\*jjyoh@snu.ac.kr

**ABSTRACT:** This paper presents an attempt to chemically separate the overlapping latent fingerprint using multivariate data analysis. More than 1 million LIBS spectra in Regions I,II,III are stored in the x-y coordinate system for generating two dimensional chemical distribution. The main emission lines of high signal-to-noise ratio (SNR) such as Fe, Al, Mg, Na, Ca, and K are used in the principal component analysis (PCA) for initial clustering of two fingerprints of different individuals. Then the classification via SIMCA (Soft-Independent Modeling Classification Analogy) and PLS-DA (Partial Least-Square Discriminant Analysis)) is applied to the same x-y positions in the overlapped Region III for reconstruction of each fingerprint, namely Region I and II as shown in the figure C. The resulting classification retains an accuracy of 90 % for SIMCA and 96.66 % for PLS-DA. Therefore, one can expect to reliably separate the overlapping fingerprint images obtained from the LIBS spectra from a two-dimensional aluminum plate.

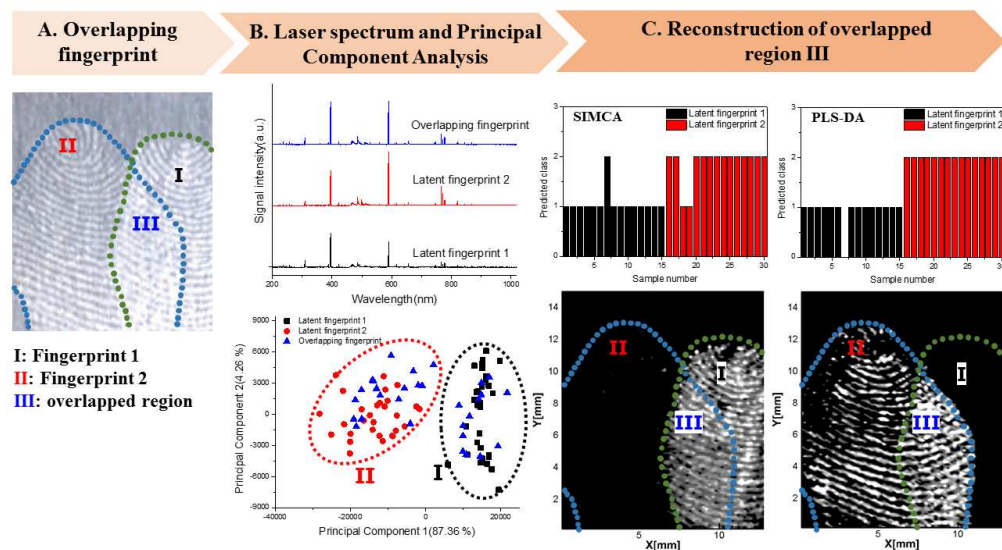


Figure. Reconstruction process for overlapping latent fingerprint on aluminum plate



## Analysis techniques for multicomponent samples in forensic fields

Marek Kotrlý <sup>\*A</sup>, Radka Šefců <sup>B</sup>

<sup>A</sup> Institute of Criminalistics Prague (ICP), Czech Republic; Charles University in Prague, Faculty of Science, Praha, Czech Republic.; <sup>B</sup> National Gallery in Prague, Staroměstské nám. 12, Prague, Czech Republic.

\*marek.kotrlý@pcr.cz

**ABSTRACT:** Most forensic analyses focus on identification, description and comparison of virtually any phase that may come in contact with humans or objects. In general, forensic laboratories would handle both natural materials as well as any materials resulting from human activity. As regards inorganic materials, laboratories most often combine the SEM / EDS / WDS / EBSD / CL methods with optical microscopy in transmitted and reflected light and fluorescence, XRF / mXRF, Raman spectroscopy/FTIR, XRD / mXRD, and others. It is important to note that the methods are by large non-destructive and the samples examined therefore retain their full value for further evidencing of the case.

- **Methodology:** In forensic analysis, is often encountered a multi-component samples, which may often require special techniques to confirm presence of some of their components. In the case described below, this concerned identification of bismuth, which was used rather unconventionally in the red layer of polychrome under gilding and silvering layers on an altar in the Krivoklat Castle chapel (around 1480-1490) in the region of Central Bohemia, the Czech Republic. The use of bismuth was documented by the X-ray fluorescence method. This surprising result led to a complex research of the altar, focusing on the layered structure and the method by which bismuth was applied to the metal-coated fields. For the overall screening of the target sample, the optical microscopy was used, followed by SEM techniques and mapping of individual elements. Moreover, they performed a phase analysis by XRD micro-diffraction, which allows an analysis from area approximately 100µm and enables for identification of a similar objects as other microscopic methods. It can be also used to analyse individual grains of pigments in the colour layer. The XRD technique becomes an irreplaceable one especially in cases when it is necessary to interpret phases which are indistinguishable by the chemical analysis. For an accurate determination of the surface to be analysed, is used an image analysis, where they transfer the XRD spot of the primary beam to an overlay image and the image from the sample in the live image. They can therefore adjust heterogeneous samples very precisely. To fasten microfragments, is used a special diffraction zero background mono-crystalline silicon plate, which was cut in orientation (100). To verify the presence of exotic Bi phase, was used another independent technique - the orthogonal TOF-SIMS FIB. Systems of time-of-flight secondary ion mass spectroscopy (TOF-SIMS) represent a new potential in forensic electron microscopy. These systems are now available as attachments to dual SEM / FIB. Compact extraction orthogonal time-of-flight instrument with a 0.5 m nominal drift length, including the reflectron was used. For the analysis, was selected a part of the scanned area (10,0 x 10,0 µm) and the primary ion beam energy was 500 pA. The 3D volume element mapping was performed. In the detailed TOF-SIMS mass spectrum was identified peak Bi (mass 209) and limits of integration.

- **Conclusions:** The methods selected are complementary to the standard ones and allow for verification of analytical findings by other, in principle independent, methods. This is especially important in the forensic science, since the experts' findings and conclusions are often used by the law enforcement bodies in their determination of guilt and related criminal sentence.

This work has been supported by the projects of the Ministry of the Interior of the Czech Republic: VG20102015065, VF20112015016, VI20152020035, VI20172020050.

*Vapor Generation &  
Sample Introduction Techniques Session*  
***VaporGeneration***

(Wed. 14<sup>th</sup> of June, h. 11.15-13.00)

## Hydride Atomizers for Atomic Absorption and Atomic Fluorescence Spectrometry - New Horizons

Jiří Dědina<sup>\*A</sup>, Jan Kratzer<sup>A</sup>, Adam Obrusník<sup>B</sup>, Marek Talába<sup>B</sup>, Pavel Dvořák<sup>B</sup>

<sup>A</sup>Institute of Analytical Chemistry of the CAS, v. v. i, Veveří 97, 602 00 Brno, Czech Republic; <sup>B</sup>Department of Physical Electronics, Faculty of Science, Masaryk University Brno, Czech Republic.

\*dedina@biomed.cas.cz

**ABSTRACT:** Hydride generation (HG) involves separation from the sample matrix and high efficiency analyte transfer from the sample to the spectrometer. In addition, it makes analyte preconcentration easy. All these factors result in a superior sensitivity. HG is therefore ideally suited for trace and ultratrace element and speciation analysis of hydride forming elements. Consequently, atomic absorption (AAS) or atomic fluorescence spectrometry (AFS) with HG can substitute or even surpass conventional approaches to element and speciation analysis based on the liquid phase sampling inductively coupled plasma mass spectrometry which generally serves as a trademark of unparalleled sensitivity. To make use of the full potential of HG-AAS(AFS) the final step of the whole procedure, hydride atomization, has to be optimized. Hydride atomization in the most often employed atomizers, quartz tubes and flames, proceeds via analyte interaction with hydrogen radicals (H radicals). Moreover, free analyte atoms are stable only in the presence of an excess of H radicals so that the distribution of H radicals in an atomizer controls the distribution of free analyte atoms and, consequently, the observed AAS or AFS signals. Therefore, the best way to optimize the atomization step is to establish how the relevant operation parameters influence the distribution of H radicals.

There is a way to quantify H radical distribution in hydride atomizers - two photon absorption laser induced fluorescence (TALIF). The other approach to quantify distribution of not only of H radicals but also of all species in atomizers is a numerical model of the gas dynamics, chemical reactions and heat transfer within the atomizers. The gas dynamics model is based on solving Navier-Stokes equations self-consistently with diffusion equations for individual components. It captures the complex three dimensional gas flow pattern in atomizers, mixing of the gases with ambient air outside of atomizers as well as potential back-diffusion of air into atomizers. The chemistry model provides spatial distribution of concentrations of a number of species involved in the atomization process. As an example, determination of H radical distributions in two different hydride atomizers, an externally heated quartz tube and a dielectric barrier discharge, under various relevant experimental parameters will be demonstrated. The determined H radical distributions will be compared with results of the numerical model. The satisfactory agreement of the results of the both approaches, TALIF experiments and numerical model, will be discussed. Outlooks of this exciting approach to atomizer optimization and to further investigation of mechanism of hydride atomization will be outlined.

This work was supported by Czech Science Foundation (P206/17-04329S), Institute of Analytical Chemistry of the CAS, v. v. i. (project no. RVO: 68081715) and by project LO1411 (NPU I) funded by Ministry of Education, Youth and Sports of Czech Republic. AO is Brno PhD Talent scholarship holder funded by Brno city municipality.

## Recent developments in the determination of inorganic anions by gas chromatography mass spectrometry

Enea Pagliano\*<sup>A</sup>

<sup>A</sup>National Research Council of Canada, 1200 Montreal Road, ON K1A 0R6 Ottawa, Canada.

\*enea.pagliano@nrc-cnrc.gc.ca

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**ABSTRACT:** The determination of inorganic anions by gas chromatography relies on derivatization chemistries able to convert the analytes in stable and volatile species. Triethyloxonium ( $\text{Et}_3\text{O}^+$ ) salts have been applied to react – in aqueous medium – halides, cyanide, thiocyanate, sulfate, nitrite, and nitrate in the corresponding alkyl-derivatives:  $\text{EtF}$ ,  $\text{EtCl}$ ,  $\text{EtBr}$ ,  $\text{EtI}$ ,  $\text{EtCN}$ ,  $\text{EtSCN}$ ,  $\text{Et}_2\text{S}$ ,  $\text{EtONO}$ , and  $\text{EtONO}_2$ . Such compounds are volatile and readily separated from the matrix under gaseous form. This key-feature of the method results in baseline clean chromatography even for complex matrices such as biological fluids, seawater, and food extracts. Samples require little preparation and derivatization is achieved at room temperature by adding an aqueous solution of  $\text{Et}_3\text{O}^+[\text{BF}_4]^-$  directly to the sample. A stable  $\text{Et}_3\text{O}^+[\text{BF}_4]^-$  solution could also be prepared and stored in acetonitrile at  $-20\text{ }^\circ\text{C}$ . The method has found applications for the measurement of halides in natural waters, nitrite and nitrate in seawater, thiocyanate in saliva, nitrate in leafy vegetables. Despite the method offering potential for quantitation at the part-per-billion level, each application was optimized for the expected analyte level in the matrix sample. In this regard, quantitation in the low  $\mu\text{M}$  was obtained for  $\text{NO}_2^-$  and  $\text{NO}_3^-$  in seawater, in the mM range for both  $\text{SCN}^-$  in saliva and  $\text{NO}_3^-$  in vegetable extracts with chromatographic runs of 1.8 min for this last case. The use of the method in conjunction with isotope dilution calibration allowed SI-traceable measurements with precision at percent level. The method is simple to implement and can resolve matrices that are usually difficult for classic methods like ion chromatography. For these reason this method has the potential for becoming a reference for the determination of inorganic ions and can be applied for the characterization of Certified Reference Materials.

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## Dielectric Barrier Discharge Atomizers of Volatile Species for Atomic Spectrometry: Applications and Mechanisms

Jan Kratzer\*, Stanislav Musil, Milan Svoboda, Jiří Dědina

Institute of Analytical Chemistry of the CAS, v. v. i., Veverří 97, 602 00 Brno, Czech Republic;

\*jkratzer@biomed.cas.cz

*Some elements, including those highly important from the toxicological or biological point of view, can be converted to volatile compounds prior spectrometric detection employing volatile species generation (VSG). VSG enhances sample introduction efficiency into spectrometric detector and thus improves detection limits and reduces risk of interferences. Chemical generation of hydrides (HG) is the most common approach to VSG, whereas atomic absorption spectrometry (AAS) with externally heated quartz tube atomizers (QTA) is the most frequent detector. Recently, various applications of miniature atmospheric plasma devices based on dielectric barrier discharges (DBD) to atomic spectrometry have been reported. In connection with VSG, DBDs are usually used as atomizers in AAS and atomic fluorescence spectrometry (AFS), excitation devices in atomic emission spectrometry (AES), but they may serve even to generate the volatile species. The aim of this work was to i) find optimum atomization conditions for selected volatile species in a DBD atomizer using AAS as a detector, ii) compare the performance of DBD atomizers to QTAs, iii) study the possibility of in-situ preconcentration of volatile species in DBDs and iv) investigate atomization mechanism of volatile species in DBDs.*

*Atomization of six hydride forming elements (As, Se, Sb, Bi, Pb and Sn) as well as of two other volatile species of Ag and Ni, generated chemically or photochemically, has been optimized in detail using a planar configuration of DBD atomizer with AAS detection. Subsequently, the performance of the novel DBD atomizer was compared to that of the routine QTA in terms of detection limits, resistance to interferences, etc. A simple in-situ preconcentration procedure of volatile species in the DBD was developed and optimized when the trapping and volatilization processes are controlled only by a presence and absence of oxygen in the discharge gas, respectively. Preconcentration efficiency of 100 % was observed for As and Sb allowing decreasing the detection limit to 0.01 and 0.02 ng mL<sup>-1</sup>, respectively, employing 300 s preconcentration period. In-situ preconcentration of Se in a DBD was studied by means of <sup>75</sup>Se radioactive indicator to find spatial distribution of trapped selenium species and quantify the capacity of the DBD to trap and release Se species. Mechanism of volatile species atomization in the DBD was explored. The role of hydrogen radicals during atomization in a DBD was found to be crucial. The DBD atomizers have been found to be the promising alternative to QTAs. In-situ preconcentration in DBDs opens a way to extremely low detection limits. Mechanism of atomization has been partly understood.*

*This work was supported by the Czech Science Foundation (project no. P206/14-23532S and P206/17-04329S) and Institute of Analytical Chemistry of the CAS, v. v. i. (Institutional Research Plan, project no. RVO: 68081715).*

## Cleavage of As–C Bond during Chemical Hydride Generation

Karel Marschner<sup>\*A,B</sup>, Stanislav Musil<sup>A</sup>, Jiří Dědina<sup>A</sup>

<sup>A</sup>Institute of Analytical Chemistry of the CAS, v. v. i., Veveří 97, 602 00 Brno, Czech Republic; <sup>B</sup>Department of Analytical Chemistry, Charles University, Albertov 8, 128 43 Prague, Czech Republic.

\*karel.marschner@biomed.cas.cz

**ABSTRACT:** Chemical hydride generation (HG) is a popular sample introduction technique in analytical atomic spectrometry. It is based on the reaction of analyte (arsenic species) with tetrahydridoborate(1–) (THB) in acidic media. Products of this reaction are volatile arsanes. Only corresponding volatile arsanes were assumed to be the products of this reaction [i.e. AsH<sub>3</sub> from arsenite and arsenate, CH<sub>3</sub>AsH<sub>2</sub> from monomethylarsonate (MAs<sup>V</sup>), (CH<sub>3</sub>)<sub>2</sub>AsH from dimethylarsinate (DMAs<sup>V</sup>), and (CH<sub>3</sub>)<sub>3</sub>As from trimethylarsine oxide (TMAs<sup>V</sup>O)]. In this work, non-corresponding volatile products of MAs<sup>V</sup>, DMAs<sup>V</sup>, and TMAs<sup>V</sup>O were observed using a batch hydride generator with a cryogenic trap connected to an atomic fluorescence spectrometer (AFS). A pronounced demethylation of MAs<sup>V</sup>, DMAs<sup>V</sup>, and TMAs<sup>V</sup>O was clearly found during HG in the media of hydrochloric, perchloric, and sulfuric acid, while HG in the medium of acetic acid or TRIS buffer (with or without prereduction with L-cysteine) lead to formation of corresponding arsanes only. An interesting situation was observed with nitric acid, in the case of MAs<sup>V</sup> and DMAs<sup>V</sup> only corresponding arsanes were observed, while in the case of TMAs<sup>V</sup>O demethylation was observed again. The extent of demethylation strongly depends on the concentration of acid and THB. By partial hydrolysis of THB with acid the demethylation effect can be almost completely suppressed. It appears that the demethylation is due to the action of first and second hydrolytic products of THB. This behavior can jeopardize accuracy of arsenic speciation analysis based on generation of substituted hydrides which has been used in some toxicological studies. [1] On the other hand, the ability to cleave As–C bond can be used for HG of more complicated arsenic species - arsenosugars (dimethylarsinoylribosides). Two hydride generators were tested for this purpose: batch, and flow injection. Our preliminary results suggest that it is much easier to generate arsanes from the arsenosugar (phosphate-ribose) in the batch generator, with the maximum HG efficiency of 68 ± 1%, than in the flow injection mode (29 ± 3%). The hydride generator in the flow mode can be however simply used for arsenic speciation in algae by postcolumn hydride generation approach and detection by AFS. With the help of arsenic speciation in water extract of algae determined by HPLC–ICP–MS we estimated the hydride generation efficiency of four major arsenosugars, which can be found in algae (glycerol, phosphate, sulfate and sulfonate) as 13 ± 1%, 28 ± 2%, 31 ± 3%, and 17 ± 1%, respectively. The limits of detection of HPLC–HG–AFS were estimated as 0.101, 0.024, 0.032, and 0.048 µg/g, for glycerol, phosphate, sulfate and sulfonate arsenosugar, respectively.

**REFERENCES:** [1] K. Marschner, S. Musil, J. Dědina, *Anal. Chem.* **88** (2016), 6366–6373.

**ACKNOWLEDGEMENTS:** Czech Science Foundation (project no. P206/17-04329S), Institute of Analytical Chemistry of the CAS, v.v.i. (project no. RVO: 68081715), Ministry of Education, Youth and Sports of the CR (Program Kontakt II. project No. LH15174), Charles University (project SVV)

## Pulsed Laser Ablation in Liquids as Digestion Method for Inductively Coupled Plasma Optical Emission Spectroscopy.

Janina Schlag<sup>A</sup>, Sven Reichenberger<sup>B</sup>, Galina Marzun<sup>B</sup>, Stephan Barcikowski<sup>B</sup>, Jürgen Schram<sup>\*A</sup>

<sup>A</sup>Instrumental Analytical and Environmental Chemistry, Niederrhein University of Applied Sciences, Frankenring 20, D-47798 Krefeld, Germany; <sup>B</sup>Instrumental Analytical Chemistry, University of Duisburg-Essen, Universitätsstr. 7, D-45141 Essen, Germany.

\*schram@hs-niederrhein.de

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**ABSTRACT:** In instrumental analysis there is a variety of different analytical methods, which can be used depending on the corresponding analytical task. However, especially in case of solids analysis without sample preparation / - digestion, the most suitable of these validatable methods are worthless. As most systems handle with liquid samples, a time consuming digestion is often unavoidable. The system used in this study, the Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), requires the input of liquid or gaseous samples.

The laser ablation into the gas phase is an already known entry method for spectroscopic methods (e.g. LA- ICP-MS) for solid samples and particles in gases, respectively.

The new approach of this study is to investigate, whether the laser ablation into liquids is a useful sample preparation technique. Therefore, a technique, which is recently used to produce nano particles for catalytic purposes, is taken into focus as sample introduction / preparation technique. We investigated first time, if this method is a universal approach to transform solids into Nano-suspension samples representatively. The resulting nanoparticle suspensions can be used as a fast and easy alternative, for time- and resource-saving digestion method for ICP-OES.

This PLAL-sample introduction Technique (Pulsed Laser Ablation into Liquids) produces an analytical sample representative solution, which allows analysis of solid samples. In opposite to classical Laser ablation into (Ar) gas phase, the ablation process can be timely and locally separated from the analytical instrument.

This study focused on following questions: Can the method of laser ablation into liquids using a flow cell be used as an alternative to a traditional chemical digestion? Is there a correlation between composition and concentration of the resulting nanoparticle suspension with conventional analysis of solids? Which conclusions can be drawn towards the chemical composition of the produced nanoparticle suspension from the composition of the sampled metal?.

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## Correlation between Gas Temperature and Atomization Behavior of Analyte Elements in Flame Atomic Absorption Spectrometry Estimated with a Multi-Wavelength High-resolution Spectrometer.

Yusuke Toya, Toshiko Itagaki, Kazuaki Wagatsuma

Institute for Materials Research, Tohoku University, 980-8577, Japan.

\*wagatuma@imr.tohoku.ac.jp

**ABSTRACT:** In flame atomic absorption spectrometry, the gas temperature for air-acetylene and nitrous oxide-acetylene flames was estimated based on a two-line method by using a simultaneous multi-wavelength spectrometer, on which a line pair of ruthenium having different excitation energies was measured at the same time. The atomization behavior of iron and ruthenium, which could be deduced from a variation in their absorption signals, was considered to be dependent not only on the gas temperature but on reducing atmosphere of the flame gas. The nitrous oxide - acetylene flame was more suitable for the simultaneous measurement because a boarder optical path having a constant and higher temperature was obtained

Flame atomic absorption spectrometry (FAAS), which is suitable for quantification of elements in solution samples, is extensively employed in various application fields: for instance, metal, chemical and food industries, biological samples, and environmental assessment. Recently, a new-type apparatus for AAS was commercialized and began to be employed, where a spectrometer system comprised a xenon-lamp continuum light source and an Echelle-type spectrograph to conduct a sequential multi-wavelength detection, thus enabling a simultaneous measurement of several absorption lines over a certain wavelength range. Due to its performance, a measurement for the two-line method can be easily conducted, where two absorption lines having closer wavelength values are simultaneously measured and then the gas temperature can be calculated from their absorbances.

In this study, the gas temperature of chemical flames for FAAS was in-situ estimated with a two-line method when an air - acetylene and a nitrous oxide - acetylene flame were employed as the atomization source [1]. A line pair of ruthenium, Ru I 372.692 nm and Ru I 372.803 nm having different excitation energies, was applied to the measurement of the gas temperature. The atomization behavior of iron and ruthenium, whose oxides had different thermodynamic properties, was investigated using the gas temperature. The fuel/oxidant ratio of both the flames as well as the height of the optical path was varied as an experimental parameter. In the nitrous oxide - acetylene rather than the air - acetylene flame, a boarder optical path having a constant/higher temperature was obtained, contributing to formation of analyte atoms with a stable atomization efficiency and thus applicable to the actual analysis in FAAS.

### Reference

[1] Y. Toya, T. Itagaki, K. Wagatsuma: *Spectrochim. Acta Part B*, 125, (2016), 146–151.

# *Chemometrics Session*

## ***Chemometrics***

*(Wed. 14<sup>th</sup> of June, h. 11.00-12.45)*

## Experimental designs in LIBS

Jean-Baptiste Sirven\*, Maria El Rakwe

Den – Service d’Etudes Analytiques et de Réactivité des Surfaces (SEARS), CEA, Université Paris-Saclay, F-91191, Gif sur Yvette, France

\* [jean-baptiste.sirven@cea.fr](mailto:jean-baptiste.sirven@cea.fr)

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*ABSTRACT: Like for any analytical technique, LIBS measurements involve many experimental parameters which can be categorized in two groups. The first one includes instrumental parameters, i.e. those that one is led to select when designing a LIBS system, related to the laser (wavelength, pulse duration, repetition rate), the beam focusing optical system, the plasma light collection setup, the spectrometer and the detector. The second group encompasses parameters of the measurement, i.e. the ones the user has to adjust when analyzing a sample: pulse energy, lens-to-sample distance (LTSD), number of laser shots, nature and pressure of the ambient medium, time gate delay and width of the detection system. Among all those parameters, it is important to underline that only that of laser ablation can be freely chosen by the user. All other ones are driven by the sample nature and by the plasma properties. Another important thing is that in general, parameters are coupled and non-linearly influence the LIBS signal. As an example, the optimum gate delay for maximum signal-to-noise ratio depends on the pulse energy, and the signal-to-noise ratio is not linear with the gate delay. Therefore, optimization of a LIBS measurement is not straightforward, and parametric studies often implemented are not sufficient to take into account those coupling and non-linearities. Finally, the optimization also depends on the analytical objective and must consider the constraints of the application.*

*Experimental designs are efficient tools for screening and optimization of influent parameters of a measurement, using a minimum number of experimental trials. Although they are broadly used in many fields of analytical chemistry, they are not so widespread in the LIBS community. In this talk, we will first review the applications of experimental designs in LIBS, generally focused on empirical optimization of an analytical response. Then, we will show how experimental designs can be useful to address other issues such as the investigation of the relationship between physical and analytical features of the measurement, the choice of the best analytical line, and the evaluation of the robustness of a LIBS system.*

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## **Support vector machines for the classification and quantification of borosilicate glass samples using Laser Induced Breakdown Spectroscopy (LIBS)**

Praveen Devangad\*, V.K. Unnikrishnan, M. Yogesha, M. M. Tamboli, K. M. Muhammed Shameem and C. Santhosh

Department of Atomic and Molecular Physics, Manipal University, Manipal-576104, India

\*praveen17dev@gmail.com

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*ABSTRACT: Laser Induced Breakdown Spectroscopy (LIBS) system has been used to classify and quantify the borosilicate glass samples. Q-switched Nd:YAG laser has been used to record fifteen LIBS spectra from each borosilicate glass sample at ambient conditions. The samples used here are similar to the matrix of simulated nuclear waste where Mn concentration is varying from 0.77 to 11.61 wt%. Three different wavelength regions of the LIBS spectra have been investigated to carry out the classification and quantification. Advanced statistical tool such as support vector machines have been employed and the best classification has been observed in all the three regions including the location with minimum number of Mn lines. The recorded spectra were divided into training set and test set. The calibration curve obtained for training set using support vector regression (SVR) with 10 segment cross validation provided  $R^2$  close to 1. Further, root mean square error of calibration (RMSEC) was found to be 0.50 wt% for training set. The performance of the calibration curve was investigated for the unknown spectra as well. The results presented here demonstrate the use of such advanced statistical tools for the future applications in nuclear waste management using LIBS technology.*

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# Likelihood based Compressive Spectrum Processing for Classification of Same-base Alloys by Laser-induced Breakdown Spectroscopy

Hyemin Jang, Sungho Shin, Sungho Jeong, Euseok Hwang\*

School of Mechanical Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, Korea.

\*euseokh@gist.ac.kr

**ABSTRACT:** In this study, a novel spectrum processing scheme is proposed for alloy classifications by laser-induced breakdown spectroscopy (LIBS). LIBS shows potential for fast and accurate identification of the material by examining the emission spectrum peaks associated with the containing elements. However, conventional peak based approach may show limited performance when the test classes share core elements, like alloys of the same base. In order to enhance performance of the same-base alloy classification, likelihood based scheme is proposed in this study. The set of candidate wavelengths are selected by the smallest cross-over error rate with the Gaussian fitted empirical probabilities or likelihoods, and the set of most influential combination is extracted sequentially by examining the conditional mutual information measure. In this way, the selected a few wavelengths contain more information for classification than the conventional dominant peaks associated with the core elements, and, consequently, the classification accuracy can be improved even for same-base alloys. Note that the proposed spectrum processing is compressive since only small part of the spectrum is used for accurate classification. The proposed scheme is evaluated with 700 LIBS captured spectra, evenly from 6 NIST's standard reference materials (SRM) of copper base alloys, SRM-1107, 1110 ~ 1114, and a Brammer Standard's BS110B. Based on the likelihood analysis, 10 wavelengths are selected out of 12,288 points of 187 ~ 1,045 nm range as illustrated by the red triangles in Fig. 1 (a), which differ from the conventional peak locations denoted with blue circles. Classification accuracies are evaluated with the 10 wavelengths of the 700 spectra by the principal component analysis (PCA) and linear discriminant analysis (LDA), which are repeated 100 times with randomly assigned 90% training and 10% testing sets. The resulting classification accuracy of the proposed scheme is 96.53 %, which outperforms the results with the 10 main peaks showing 86.84% and the 12,288 full points showing 90.19%. The classification accuracy variation as a function of no. of selected wavelengths are plotted in Fig. 1 (b). As discussed, the edges of the minor peaks selected in the proposed scheme contain more information for the same-base alloy classification than the main peaks in information theoretic sense, which enables the proposed likelihood based scheme to achieve improved classification accuracy with a few wavelength points or compressed partial spectra.

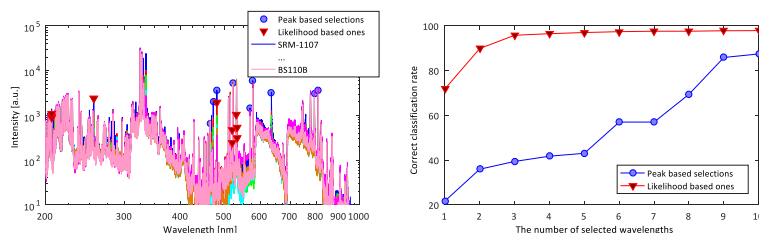


Fig. 1. LIBS captured spectrum of SRM-1107 copper base alloy with the proposed wavelengths in red triangles and main peaks in blue circles (a) and classification accuracies as a function of no. of selected wavelengths (b).

**Acknowledgement:** This study was supported by the R&D Center for Valuable Recycling (Global-Top R&BD Program) of the Ministry of Environment. (Project No.: 2016002250003)

## Utility of Machine-Learning Enabled LIBS in Forensic Analysis of High Level Nuclear Waste

Onkangi Nyairo Joshua<sup>\*A</sup>, Maina David<sup>A</sup>, Kalambuka Hudson Angeyo<sup>B</sup>

<sup>A</sup> Institute of Nuclear Science & Technology, University of Nairobi, P.O Box 30197 Nairobi, Kenya;

<sup>B</sup> Department of Physics, University of Nairobi, P.O Box 30197 Nairobi, Kenya.

\* joshuanyairo@students.uonbi.ac.ke

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**ABSTRACT:** Illicit diversion and use of nuclear and radiological materials (NRM) has been on the rise since the fall of the Soviet Union. Trafficking of NRM and high level nuclear wastes in concealed form (in vitrified glass, mixed with powders and even dissolved in liquids) by terrorist groups for malicious intentions such as making radiological dispersal devices and improvised nuclear devices requires to be timely detected. There is therefore need to fully interrogate every step in the nuclear fuel cycle to publish every new detected signature generated and create a reference database for use in nuclear forensics investigations and attribution. As such, compared to existing classical methods that are invasive, destructive and require sizeable sample and tedious sample preparations (dissolution digestion and separation of matrix that would generate more radioactive wastes that require specific procedures for disposal or proper storage), more rapid state-of-the art techniques are desirable. Laser induced breakdown spectroscopy is one of such technique. As it overcomes such limitations and is particularly useful in analysis in radioactive environments due to its stand-off analysis capability. We investigated LIBS for direct rapid analysis of nuclear fission products in the context of nuclear forensics. The goal of this work was to develop models for qualitative and quantitative detection of FP in high level nuclear wastes. Vitrified glass was simulated by preparing fused glass beads spiked with nuclear fission products (FP) (Y, Rb, Sr and Zr) (at concentrations typical to their occurrence in spent nuclear fuel). The fused glass beads were analyzed by feature selection peak-free LIBS utilizing an artificial neural network (ANN) multivariate quantitative model developed for the task. Classical LIBS suffers from high detection limits and the limitation of peaks from low concentration elements getting buried in the background continuum. Model pellet and liquid forms of high level nuclear waste were also prepared and similarly analyzed. A comparison was made between different neural network architectures namely; cascade correlation (newcf) and feed forward back propagation (newff) algorithms to realize the best performing architecture for quantitative analysis. Results show that newff algorithm performs better: The relative error of prediction (REP) was found to be < 15%. Model performance was best for liquid samples (REP=3.8%) as opposed to pellet and glass beads. The corresponding explained variance ( $R^2$ ) were above 95% for most of the models developed. The detection limit for liquid samples was 6 - 8 ppm, 20 - 100 ppm for pellet and >100ppm for fused glass. Support vector machine was used to successfully discriminate the samples based on the contribution of the FP. This has a significance in attribution since occurrence of this FP in specific amounts and pattern could infer source provenance. The two analytical models (trace quantitative and qualitative multivariate exploratory) can be embedded into the software interfaces of portable/handheld LIBS systems and assist rapid analysis and detection of fission products in materials whose origin is suspected to be from the back end of the nuclear fuel cycle or to perform proliferation/safeguards monitoring of FP in the environment as a result of nuclear activity. For liquids only 2 $\mu$ l is required as a coat on a suitable substrate while for solid (glass, powder) materials only tiny mm size fragments are required.

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## Application of Conditional Analysis to the Quantification of Au in Ores by Laser-Induced Breakdown Spectroscopy.

Daniel Diaz<sup>\*A</sup>, David W. Hahn<sup>B</sup>, Alejandro Molina<sup>A</sup>

<sup>A</sup>Facultad de Minas, Universidad Nacional de Colombia- Sede Medellin, Cra. 80 #63-223 Medellin, Colombia;

<sup>B</sup>Department of Mechanical and Aerospace Engineering, University of Florida, Gainesville, Florida 32611, USA.

\*dhdiazo@unal.edu.co

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**ABSTRACT:** Laser-induced Breakdown Spectroscopy (LIBS) together with conditional analysis methodology was applied for the first time to a solid Au-bearing ore with the purpose of exploring its application as an in situ and online monitoring technique for the precious metal mining industry. Au-bearing ores and surrogates samples with a gold concentration varying from 0.5 to 35.1  $\mu\text{g/g}$  and 0-375  $\mu\text{g/g}$ , respectively, were prepared as pressed pellets and analyzed with a conventional LIBS setup that included a 1064 nm Nd:YAG laser, a Czerny-Turner spectrograph, an ICCD camera and an optical setup configured to collect the plasma light in backscatter mode. 100-single shot spectra of ore samples did not present Au emission signals. Contrary, surrogate samples presented Au signals that yielded Au detection limits of 1.1  $\mu\text{g/g}$ . Evidence that increasing the number of sampling pulses over the ore samples increased the number of single shot spectra containing Au emission lines, as well as the fact that scanning electron microscopy of ore samples showed that gold was present as discrete and sparse entities in ores, suggested that during ore analysis the frequency for successful Au detection was low. Assuming that LIBS sampling rates for Au particles follow a Poisson distribution, LIBS particle sampling rates were calculated for Au concentrations of 1.1  $\mu\text{g/g}$  and 10.0  $\mu\text{g/g}$  as 0.04% and 0.32%, respectively. These low sampling rates justified the use of conditional analysis to detect Au in ores. The application of Monte Carlo simulations to conditional analysis indicated that around 100 gold-containing particles should be sampled to accurately represent the discrete nature of gold in the ore. Despite the large number of laser shots (more than  $10^5$ ) needed to sample 100 gold-containing particles, Au measurement at concentrations as low as 1  $\mu\text{g/g}$  was achieved after application of conditional analysis to ore samples that withstood a total of 5000 sampling shots. Results are encouraging and illustrate the applicability of LIBS to Au in field semi-quantitative analysis.

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# *Clinical and Pharma Sessions*

## ***Pharma I***

*(Thu. 15<sup>th</sup> of June, h. 9.15-10.45)*

## **Cancer Diagnosis using LIBS and Machine Learning Tools: Progress and Challenges.**

Noureddine Melikechi\*, Rosalba Gaudioso, Ebo Ewusi-Annan

Department of Physics and Applied Physics, University of Massachusetts Lowell, USA

\*Noureddine\_Melikechi@uml.edu

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*ABSTRACT: Cancer refers to a class of diseases that is triggered by abnormal cell growth in one organ with the potential to spread other parts of the body. Despite numerous research and development efforts, cancer remains a challenging disease to diagnose and treat. Worldwide, it is the second leading cause of death and was responsible for nearly 1 in 6 deaths, or 8.8 million deaths, in 2015. Early diagnosis is crucial to increase the survival rate and quality of life of cancer patients. Thus, developing non-invasive screening methods would represent a major advance towards large scale screening and prevention of asymptomatic tumors such as Epithelial Ovarian Cancer (EOC) and other types of cancer. By combining femtosecond LIBS with unsupervised classification techniques, we have shown that it is possible to discriminate blood samples extracted from healthy and diseased mice with an accuracy that approaches 80%. We will present our most recent results and in particular will report on the effects of various substrates on which LIBS measurements are performed on the classification accuracy of blood samples extracted from cancerous and healthy mice.*

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## ICPMS-Based Quantitative Analysis of Glyco-PTMs via Metabolism-Mediated and Clickable Lanthanide-Tagging Strategy

Yong Liang<sup>A</sup>, Limin Yang<sup>A</sup>, Qiuquan Wang<sup>\*A,B</sup>

<sup>A</sup> Department of Chemistry & the MOE Key Lab of Spectrochemical Analysis and Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China; <sup>B</sup> State Key Lab of Marine Environmental Science, Xiamen University, Xiamen 361005, China.

yongliang@stu.xmu.edu.cn; lmyang@xmu.edu.cn; qqwang@xmu.edu.cn\*

**ABSTRACT:** Protein glycosylation, one of the most important and extensive post translational modifications (PTMs) of proteins, have been a research hotspot in the past several decades<sup>[1,2]</sup>. Although it is well acknowledged that the protein glycosylation are playing an important role in cell-cell interactions, related tumor metastasis processes and many other human health and diseases, acquisition of their quantitative information has yet been a challenge to date. Because of their nongene-coded complicated structures with various linkages, lower ionization efficiencies in molecular mass spectroscopy and heavy matrix disturbance, it is still a challenge to quantitatively analyze protein glycosylation using commonly used lectin-based methods and MALDI/ESI techniques<sup>[3]</sup>. In our latest report<sup>[4]</sup>, we developed an ICPMS-based glycoengineering strategies, for the first time, to visualize and quantify the cell surface sialic acids (Sias) that is one of the most important glycosylation PTMs. Using Ac<sub>4</sub>ManNAz as the sugar substrate that can be metabolically transformed and biospecifically incorporated as the cell surface terminal Sias, which could be labeled/tagged with fluorescence- and/or lanthanide-tags via copper free click reaction to realize imaging and quantification of cell surface sialic acids using confocal laser scanning microscope (CLSM) and ICPMS. Based on this method, we could obtain qualitative profiling and quantitative information of the Sias on the cell surface at the same time with the limit of detection down to 8.9 fmol. In order to push such a strategy forward to quantify more monosaccharides in a more complicated glycan chain structure for understanding their corresponding biological roles, we are now designing and synthesizing more noncanonical analogues of monosaccharide substrates and corresponding lanthanide-tags. We expect to simultaneously obtain the quantitative information on more monosaccharides in the glycan chain structure using ICPMS.

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## Determination of biomarkers in oral fluid for monitoring heart failure patients

Francesca G. Bellagambi <sup>\*A</sup>, Tommaso Lomonaco <sup>A</sup>, Silvia Ghimenti <sup>A</sup>, Valentina Barletta <sup>B</sup>, Andreina D'Agostino <sup>B</sup>, Denise Biagini <sup>A</sup>, Mario Marzilli <sup>B</sup>, Maria Giovanna Trivella <sup>C</sup>, Fabio Di Francesco <sup>A</sup>, Roger Fuoco <sup>A</sup>

<sup>A</sup> Dipartimento di Chimica, Università di Pisa, Via Giuseppe Moruzzi 13, 56124 Pisa, Italy; <sup>B</sup> Dipartimento di Patologia Chirurgica, Medica, Molecolare e dell'Area Critica, Università di Pisa, Via Paolo Savi 10, 56126 Pisa, Italy; <sup>C</sup> Istituto di Fisiologia Clinica, Consiglio Nazionale delle Ricerche, Via Giuseppe Moruzzi 1, 56124 Pisa, Italy.

\*francesca.bellagambi@dccl.unipi.it

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**ABSTRACT:** Heart failure (HF) is a complex clinical syndrome caused by a wide range of cardiovascular disorders, such as structural or functional abnormalities of the heart. The clinical status of a HF patient can be evaluated by detecting specific biomarkers of pathogenic biological processes. Beside conventional clinical investigations, oral fluid analysis have been recognized as one of the most effective, easy, painless and non-invasive ways of identifying physiological and pathophysiological conditions. This study was focused on the development and validation of analytical methods based on UHPLC-MS/MS, spectrophotometric and immunochemical techniques to determine specific salivary biomarkers. Tumor necrosis factor- $\alpha$ , interleukin-10, 8-iso-prostaglandin  $F_{2\alpha}$ , uric acid, aldosterone,  $\alpha$ -amylase, lactate and cortisol in oral fluid samples were determined. Special attention was paid to the optimization of the sampling procedures and sample handling. Each biomarker is representative of a pathological condition occurring with the HF syndrome, so that abnormal levels of these molecules could be associated with the severity and progression of the disease. The methods were then used in the framework of the H2020 HEARTEN Project and to support the development of specific biosensors able to anticipate critical exacerbation episodes by rising an alarm in hospital information systems remotely connected by an mHealth application.

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**Acknowledgement:** This work was supported by the project PHC-643694 HEARTEN, funded by the European Commission under the H2020 programme.

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## Determination of Cd and Pb in Creamy, Opaque and Shimmering Lipstick by ICP-MS

Marcia Foster Mesko<sup>\*A</sup>, Vanize Caldeira Costa<sup>A</sup>, Diogo La Rosa Novo<sup>A</sup>, Rodrigo Mendes Pereira<sup>A</sup>, Letícia Severo Fagundes Pereira<sup>B</sup>, Rochele Sogari Picoloto<sup>B</sup>

<sup>A</sup>Centro de Ciências Químicas, Farmacêuticas e de Alimentos, Universidade Federal de Pelotas, Av. Eliseu Maciel, Capão do Leão, RS, Brazil; <sup>B</sup>Departamento de Química, Universidade Federal de Santa Maria, Av. Roraima, Santa Maria, RS, Brazil.

\*marciamesko@yahoo.com.br

**ABSTRACT:** The natural occurrence in rocks, soil and water may result in the presence of toxic elements in the raw materials used to produce cosmetics, especially in mineral pigments.<sup>1</sup> The frequent use of cosmetics may expose consumers to toxic elements and, consequently, to result in localized skin problems and/or systemic effects. Several regulatory institutions have recently restricted or prohibited the use of toxic and potentially toxic elements in cosmetics.<sup>2-4</sup> Among these elements, cadmium and lead are considered of particular importance due to their toxic effects and the determination of these elements in cosmetics is still a challenge considering the complexity of these matrices. Special attention should be given to cosmetics used on body regions where absorption of potentially toxic elements may be more significant, such as lipsticks. Many analytical techniques have been used to determine Cd and Pb in lipstick, and digestion methods using mixtures containing concentrated nitric and hydrofluoric acid are commonly used for sample digestion.<sup>5-7</sup> However, the use of HF may cause damages in sample introduction systems of some equipment. Furthermore, HF has high toxicity and may cause interferences during determination step.<sup>8</sup> There are a few studies evaluating the use of other complexing acids in substitution to HF for lipstick digestion. In the present work, the use of complexing acids (HF and HCl) combined with HNO<sub>3</sub> was evaluated for the digestion of commercial lipsticks and further Cd and Pb determination by inductively coupled plasma mass spectrometry (ICP-MS). Creamy (red), opaque (brown, coral, pink, purple, red) and shimmering (brown) lipsticks produced in São Paulo state, Brazil, were homogenized in a water bath at 70 °C for 20 min. Lipstick samples (500 mg) were digested in closed vessels using HNO<sub>3</sub> (6 mL) or a mixture containing HNO<sub>3</sub> and HCl (2 or 0.5 mL) or HNO<sub>3</sub> and HF (2 or 0.5 mL). Digestion was carried out using a microwave oven (Multiwave 3000<sup>TM</sup>, Anton Paar, Austria), and the applied microwave heating program was: (i) 750 W for 10 min (ramp of 20 min) and (ii) 0 W for 20 min. The determination of <sup>111</sup>Cd and <sup>208</sup>Pb was performed using an inductively coupled plasma mass spectrometer (Elan DRC II, PerkinElmer - SCIEX, Canada). The results indicate that complexing acids are essential for subsequent determination of Pb in shimmering lipsticks. However, it was possible to obtain suitable recoveries for Pb by using HNO<sub>3</sub> combined with only 0.5 mL of HCl. Using this condition, recoveries for Cd and Pb were between 95 and 103% in all types of evaluated lipstick. Moreover, the use of HCl avoids the use of HF during the lipstick digestion and the occurrence of interferences during the determination step. The limits of detection were 2.6 and 76.7 ng g<sup>-1</sup> for Cd and Pb, respectively. The concentration of Pb in the evaluated samples ranged in a wide range (270 to 2246 ng g<sup>-1</sup>), and the highest concentration was observed in opaque lipsticks, especially in coral and pink lipsticks. In addition, Cd was only detected in opaque lipsticks (31 ng g<sup>-1</sup> in pink lipstick and 6.78 ng g<sup>-1</sup> in brown lipstick), which have a significant amount of white pigments. The higher concentration of Cd and Pb in opaque lipstick may be associated with the use of high amounts of titanium dioxide in this type of lipstick.

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# *Clinical and Pharma Sessions*

## ***Pharma II***

*(Thu. 15<sup>th</sup> of June, h. 11.15-12.00)*

## The use of X-ray fluorescence and FTIR microspectroscopy for the highly spatially resolved analysis of elemental and biochemical changes occurring in the hippocampal formation during postnatal brain development

Joanna Chwiej<sup>\*A</sup>, Marta Palczynska<sup>A</sup>, Agnieszka Skoczen<sup>A</sup>, Krzysztof Janeczko<sup>B</sup>, Christophe Sandt<sup>C</sup>, Rolf Simon<sup>D</sup>, Zuzanna Setkowicz<sup>B</sup>

<sup>A</sup>Department of the Medical Physics and Biophysics, Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Krakow, Poland

<sup>B</sup>Department of Neuroanatomy, Institute of Zoology, Jagiellonian University, Krakow, Poland

<sup>C</sup>SOLEIL, St Aubin, France

<sup>D</sup> Institut für Synchrotronstrahlung, Research Centre Karlsruhe, Karlsruhe, Germany

\*joanna.chwiej@fis.agh.edu.pl

**ABSTRACT:** Epilepsy is one of the most common serious neurological disorder [1]. According to WHO data, Europe has been estimated to have 6 million patients with active epilepsy, and the annual European health costs associated with epilepsy are over 20 billion of euros [2]. The most extreme form of the disease is status epilepticus (SE) and the incidence of SE shows a bimodal age distribution with peaks in children less than a year of age and the elderly [3-5]. However, both the incidence and recurrence of seizures is the highest in paediatric population [3-4].

Age-dependent susceptibility to epileptic seizures may reflect biomolecular changes occurring in the brain during postnatal development. Therefore, in this study, the elemental and biochemical changes taking place during the brain development in the area involved in the pathogenesis and progress of epilepsy as well as undergoing neurodegenerative changes as a result of seizures (hippocampal formation) were examined.

The biomolecular composition of hippocampal formations was studied in rats. The animals in the three periods of postnatal life (6-, 30- and 60-days-old rats) corresponding to the infancy, childhood and adult in humans were compared. To follow age-dependent elemental and biochemical changes of tissues highly spatially resolved X-ray fluorescence and FTIR spectroscopies (respectively) were applied.

The obtained results showed fluctuations of Ca, Fe and Zn levels in selected areas of hippocampal formation between 3 examined groups of rats. The biochemical analysis of tissues showed that the level of lipids including unsaturated fats increased between 6<sup>th</sup> and 30<sup>th</sup> day of rats life. The opposite relation was found for the relative content of proteins with the  $\beta$ -type secondary structure. Both elemental and biochemical changes were the most intensive in the first examined period of animals life.

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# Comparative Analysis of the Heme Iron Electronic Structure and Stereochemistry in Tetrameric Rabbit Hemoglobin and Monomeric Soybean Leghemoglobin $\alpha$ Using Mössbauer Spectroscopy with a High Velocity Resolution

I.V. Alenkina<sup>\*A</sup>, A. Kumar<sup>B</sup>, A.L. Berkovsky<sup>C</sup>, M.I. Oshtrakh<sup>A</sup>

<sup>A</sup>Institute of Physics and Technology, Ural Federal University, Ekaterinburg, 620002, Russian Federation;

<sup>B</sup>School of Biological Science, 320 Manter Hall, University of Nebraska, Lincoln, Nebraska, USA 68588;

<sup>C</sup>Hematological Research Center of the Ministry of Health and Social Development of Russian Federation, Moscow, 125167, Russian Federation

\*alenkina-ira@mail.ru

**ABSTRACT:** A comparative study of tetrameric rabbit hemoglobin (HbR) and monomeric soybean leghemoglobin  $\alpha$  (Lba) in the oxy- and deoxy-forms was carried out using  $^{57}\text{Fe}$  Mössbauer spectroscopy with a high velocity resolution in order to analyze the heme iron electronic structure and stereochemistry in relation to Mössbauer hyperfine parameters. The Mössbauer spectra of HbR in the oxy-, deoxy- and partially deoxygenated forms were fitted using two quadrupole doublets related to the  $^{57}\text{Fe}$  in  $\alpha$ - and  $\beta$ -subunits in these protein forms. In contrast, the Mössbauer spectra of Hba in the oxy- and deoxy-forms were fitted with two and three quadrupole doublets, respectively, related to two conformational sub-states in the heme distal side in the oxy-form and three conformational sub-states in the heme proximal side in the deoxy-form. Small variations of Mössbauer hyperfine parameters related to small differences in the heme iron electronic structure and stereochemistry in HbR and Lba are discussed.

It is well known that oxygen binding in various hemoglobins is related to their protein and heme iron electronic structures. The heme iron stereochemistry affects the Fe(II) electronic structure in both oxy- and deoxy-forms of hemoglobins. Larger or smaller overlap of the Fe(II) d-electrons with electron orbitals of four N atoms in the porphyrin plane and N $\epsilon$  atom of the imidazole ring of His F8 may affect the smaller or larger overlap of the Fe(II) d-orbitals with electron orbitals of O<sub>2</sub> molecule. Therefore, the Fe(II) electronic structure also plays an important role in the oxygen binding process.  $^{57}\text{Fe}$  Mössbauer spectroscopy is a powerful technique and has proved to be an excellent tool to study the Fe electronic structure in iron-containing proteins on the basis of Mössbauer hyperfine parameters. A comparative study of tetrameric rabbit hemoglobin (HbR) in the oxy-, deoxy- and partially deoxygenated forms and monomeric soybean leghemoglobin  $\alpha$  (Lba) in the oxy- and deoxy-forms was carried out. An analysis of the absorption line shape in the proteins' Mössbauer spectra in comparison with those of the standard absorber sodium nitroprusside demonstrated the complicity of the proteins' spectra required their fit using several quadrupole doublets. These doublets and their hyperfine parameters were related to stereochemical differences in the heme distal or proximal sides in HbR and Lba. This work was supported by the Ministry of Education and Science of the Russian Federation (Project No. 1959).

## Distribution of trace elements in tobacco and shisha products in Turkey and accumulation on their smoke

Gul Sirin Ustabasi<sup>A,B</sup>, Suleyman Akman<sup>A</sup>, Asli Baysal<sup>\*B</sup>

<sup>A</sup>Department of Chemistry, Faculty of Arts and Sciences, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey; <sup>B</sup> Heathy Services Vocational School of Higher Education, Medical Laboratory Technics, Istanbul Aydin University, Sefakoy-Kucukcekmece, Istanbul, Turkey

\*aslibaysal@aydin.edu.tr

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*ABSTRACT: While it was extensively investigated that toxic metals or other toxins in tobacco and tobacco smoke, there are still some lack in accumulation from products to smoke. Also especially last decades the shisha (hookah or a waterpipe) usage was dramatically increased and there have no boundary in this subject. In this work, some trace metals (Cd, Cu, Co, Ni, Zn and Pb) were determined in tobacco and shisha products and their smoke by graphite furnace atomic absorption spectrometry (GFAAS). The results were compared by accumulation from products to their smoke obtained after sample digestion. The tobacco and shisha samples were dried at 90°C for 12 h and digested using microwave-assisted wet digestion method with nitric and perchloric acids. Smoke investigation was applied in controlled box and tobacco and shisha products were burning, then their smoke collected on a filter. After collection of smoke on a filter, the filter was digested using same procedure. In order to validate methods, standard reference materials (bush branches and leaves) were used. Accumulation level evaluated for each analytes in crude products and smoke samples and statistical analysis were made using ANOVA.*

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# *Clinical and Pharma Sessions*

## ***Pharma III***

*(Thu. 15<sup>th</sup> of June, h. 14.15-16.00)*

## Flexible and disposable sensors based on graphenic materials for wound monitoring

Fabio Di Francesco<sup>\*A</sup>, Bernardo Melai<sup>A</sup>, Nicola Calisi<sup>A</sup>, Arno Kirchhain<sup>A</sup>, Federico Vivaldi<sup>A</sup>, Roger Fuoco<sup>A</sup>, Pietro Salvo<sup>B</sup>

<sup>A</sup>Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via Moruzzi 1, 56124 Pisa, Italy; <sup>B</sup>Istituto di Fisiologia Clinica, Consiglio Nazionale delle Ricerche, Via Moruzzi 1, 56124 Pisa, Italy.

\*fabio.difrancesco@unipi.it

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**ABSTRACT:** Temperature and pH are critical parameters in determining the reactivity of chemicals and their measurement is fundamental in fields such as agriculture, environmental and food science, chemistry, biology and medicine. In this work, accomplished in the framework of the SWAN-iCare project ([www.swan-icare.eu](http://www.swan-icare.eu)), we report the fabrication, testing and validation of disposable sensors, namely a resistive sensor based on reduced graphene oxide for the measurement of temperature and a potentiometric sensor based on graphene oxide for the measurement of pH in the wound bed. The term chronic wound groups different pathologies (i.e. venous leg ulcers, diabetic foot ulcers and pressure ulcers) having in common long healing times and profound impact on the quality of life for a large number of patients. For example, it is estimated that 25% of the about 33 million European citizens affected from diabetes develop a diabetic foot, a chronic ulcerative condition bringing a not negligible risk of amputation and death. The SWAN-iCARE project aims at providing the current negative pressure therapy with remote monitoring capabilities in order to improve the management of chronic wounds. In-vitro tests with model solutions and real samples demonstrated for the temperature and pH sensor accuracies of  $\pm 0.5$  °C (range 20-40 °C) and  $\pm 0.2$  pH units (range 3-10 pH units) respectively. The use of sensors in contact with the wound bed poses strict requirements in terms of biocompatibility and comfort for the patient, which are also addressed. The potential application of such low cost sensors in other fields (e.g. marine monitoring) is also briefly outlined.

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## Non-destructive spectroscopic techniques applied to dentistry research

Sofia Pessanha<sup>\*A, B</sup>, João Silveira<sup>A, C</sup>, Filipa Chasqueira<sup>A, C</sup>, João Godinho<sup>A, C</sup>, António Mata<sup>A, C</sup>, Maria Luisa Carvalho<sup>A, B</sup>

<sup>A</sup>LIBPhys -Laboratório de Instrumentação, Engenharia Biomédica e Física da Radiação; <sup>B</sup>Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal; <sup>C</sup>Faculdade de Medicina Dentária da Universidade de Lisboa, 1649-003 Lisboa, Portugal

\*sofia.pessanha@fct.unl.pt

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**ABSTRACT:** In this work, the advantages of two non-destructive analytical techniques- Energy Dispersive X-Ray Fluorescence (EDXRF) and Raman spectroscopy in the analysis of dental tissues will be discussed and several applications will be presented. Regarding the evaluation of the elemental content and  $PO_4^{3-}$  profile before and after treatment with bleaching products, three separated studies will be presented, concerning the use of different products (power bleaching, nightguard bleaching and over-the-counter) both according to the manufacturer's instructions and in an abusive manner. Results show no significant differences in elemental content of enamel before and after treatment, whereas a significant decrease in the intensity of the  $PO_4^{3-}$  profile was determined. These differences in the outcome of the two techniques may rely in a very superficial demineralization, difficult to evaluate with EDXRF. The demineralization degree was calculated in all studies and was determined to be more substantial in products with lower pH rather than with higher active principle (Hydrogen Peroxide or Carbamide Peroxide). EDXRF and Raman spectroscopy can also provide valuable information regarding the interaction of the materials used for restoration and dentin tissue – amalgam or composite fillings. In this work we used Raman spectroscopy to evaluate the performance of adhesive systems created for the use with composite fillings. Polymeric composite fillings are not capable to self-adhere to dentin so an adhesive is required to infiltrate the tooth's structure and copolymerize with the restorative material, creating a hybrid layer. The degree of conversion of monomers as well as the depth of impregnation of the adhesive throughout the hybrid layer was compared for two different adhesive systems and for sound and affected dentin. Furthermore, the analysis of teeth treated with mercury-based amalgam fillings will be presented giving evidence of the contamination of Hg throughout the dentin into the pulp chamber.

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## Determination of volatile organic compounds in human breath for monitoring heart failure patients

Tommaso Lomonaco <sup>\*A</sup>, Silvia Ghimenti <sup>A</sup>, Francesca G. Bellagambi <sup>A</sup>, Denise Biagini <sup>A</sup>, Valentina Barletta <sup>B</sup>, Andreina D'Agostino <sup>B</sup>, Doralisa Morrone <sup>B</sup>, Mario Marzilli <sup>B</sup>, Maria Giovanna Trivella <sup>C</sup>, Fabio Di Francesco <sup>A</sup>, Roger Fuoco <sup>A</sup>

<sup>A</sup> Dipartimento di Chimica, Università di Pisa, Via Giuseppe Moruzzi 13, 56124 Pisa, Italy; <sup>B</sup> Dipartimento di Patologia Chirurgica, Medica, Molecolare e dell'Area Critica, Università di Pisa, Via Paolo Savi 10, 56126 Pisa, Italy; <sup>C</sup> Istituto di Fisiologia Clinica, Consiglio Nazionale delle Ricerche, Via Giuseppe Moruzzi 1, 56124 Pisa, Italy.

\*tommaso.lomonaco@dccci.unipi.it

**ABSTRACT:** Heart failure (HF) is a complex clinical syndrome caused by a wide range of cardiovascular disorders (such as structural or functional abnormalities of the heart) and represent the main cause of mortality and poor quality of life in the western societies. According to the European Heart Failure Association, 26 million people experience HF globally and 3.6 million people are diagnosed with HF, every year. Nowadays, the common clinical approaches used to diagnose and monitor HF are based on analyzing natriuretic peptides (e.g. B-type or N-terminal pro-B-type natriuretic peptides) in serum and performing transthoracic Doppler 2D echocardiography. Beside these conventional clinical investigations, breath analysis is an extraordinarily appealing tool for a most effective, easy, painless and non-invasive monitoring of patients suffering from HF because of the chemical composition of exhaled breath reflects the physiological and pathophysiological process. The aim of this work was to develop an analytical procedure, based on Needle Trap Micro-Extraction coupled to GC-MS/MS, to determine volatile organic compounds (VOCs) in human breath. This emerging and promising technique that employ a stainless-steel needle (internal diameter 0.34 mm and length 6 cm) packed with 1 cm of Divinylbenzene, 1 cm of Carboxen 1000 and 1 cm of Carboxen 1000 allows analytes sampling and pre-concentration to be performed in a single step. Needle trap devices were automatically desorbed by a CONCEPT GC-autosampler (PAS Technology) and VOCs were analysed by a 7890B GC System equipped with a DB5ms gas chromatographic column (60 m, 0.25 mm ID, 1.0 µm) and coupled to a 7010 MS Triple Quad mass spectrometer (Agilent Technologies). The method was then used in the framework of the H2020 HEARTEN project to support the development of specific biosensors (e.g. acetone), which will be integrated into an innovative mobile platform remotely connected by an mHealth application. According to this scenario, HF patients will be able to monitor itself at home by using their smartphones.

**Acknowledgement:** This work was supported by the project PHC-643694 HEARTEN, funded by the European Commission under the H2020 programme.

## Detection and Mapping of Cutaneous Melanoma Using Laser Induced Breakdown Spectroscopy

Youngmin Moon<sup>B</sup>, Jung Hyun Han<sup>B</sup>, Jang-Hee Choi<sup>A</sup>, Sungho Jeong<sup>\*A</sup>

<sup>A</sup>School of Mechanical Engineering, Gwangju Institute of Science and Technology, 1 Oryong-dong Buk-gu Gwangju 500-712, Republic of Korea; <sup>B</sup>Department of Medical System Engineering, Gwangju Institute of Science and Technology, 1 Oryong-dong Buk-gu, Gwangju 500-712, Republic of Korea;

\*shjeong@gist.ac.kr

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**ABSTRACT:** Melanoma is the most dangerous form of skin tumor, accounting for 90% of the deaths associated with cutaneous tumors [1]. The detection of melanoma and the determination of the extent of surrounding tissue over which melanoma cells infiltrated are critical in surgical treatment of melanoma. This work reports the results of melanoma classification from normal dermis by the univariate and multivariate analyses of laser induced breakdown spectroscopy (LIBS) signals of melanoma and dermis samples. Both pellet and excised skin samples were used for the LIBS measurement. It is shown that the intensities of Mg(II) and Ca(II) signals were significantly higher in melanoma than in dermis. The sensitivity of melanoma from the multivariate analysis was as high as 0.994 and 0.967 for the pellet and excised skin samples, respectively [2]. Also, the results for elemental mapping of melanoma and surrounding dermis are shown in comparison with the image for histology analysis. The contours of LIBS intensity map matched closely with the histologically determined pigmented melanoma, melanoma border with locally developed inflammatory cells, and dermis.

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- [2] J. H. Han, Y. Moon, J. J. Lee, S. Choi, Y.-C. Kim, and S. Jeong, "Differentiation of cutaneous melanoma from surrounding skin using laser-induced breakdown spectroscopy", *Biomedical Optics Express* 7, 57-65 (2016)
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## Application of TEA CO<sub>2</sub> LIBS for Elemental Analysis of Powdered Biological Samples

Sanja Zivkovic\*, Milos Momcilovic, Jelena Savovic

<sup>A</sup>Institute of Nuclear Sciences Vinca, University of Belgrade, Serbia.

\*sanjaz@vinca.rs

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*ABSTRACT: In this work, we present a simple and cost effective LIBS (Laser Induced Breakdown Spectroscopy) method for quantitative elemental analysis of powdered biological materials based on laboratory prepared calibration samples. The proposed non-gated LIBS system uses pulsed infrared nanosecond Transversely Excited Atmospheric (TEA) CO<sub>2</sub> laser as the laser light source. The material used for the analysis was a blue – green alga Spirulina (Arthrospira Maxi- ma), commercial nutritional supplement widely used in food and pharmaceutical industries. Analytical curves for Ba, Fe, Mg, Mn and Sr were constructed using laboratory produced matrix-matched calibration samples. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used as the reference technique for elemental quantification, and reasonably well agreement between ICP and LIBS data was obtained. The estimated limits of detection of detection are comparable to those reported in literature. Results confirm that, in respect to its sensitivity and precision, proposed TEA CO<sub>2</sub> laser based LIBS method can be successfully applied for quantitative analysis of macro and micro-elements in powdered samples. The main advantage of the proposed method is its simplicity and potential for future applicability to quantitative analysis of a broad range of powder materials.*

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## Comparison of selected calibration approaches in LA-ICP-MS studies of Mg and Zn distribution in rat brain tissue

Natalia Miliszkiewicz<sup>\*A</sup>, Stanisław Walas<sup>A</sup>, Anna Tobiasz<sup>A</sup>, Emilia Grygo-Szymanko<sup>A</sup>, Danuta Dudek - Adamska<sup>A</sup>

<sup>A</sup> Department of Analytical Chemistry, Jagiellonian University in Krakow, Krakow, Poland

\*natalia.miliszkiewicz@gmail.com

**ABSTRACT:** Laser ablation technique has proved its value as a useful tool of microsampling especially when coupled to mass spectrometer and thus has been successfully applied in various analyses of precious materials like historic artefacts or human remains, as well as for imaging of elements' distribution in soft tissues.<sup>1</sup> However quantitative analysis by LA-ICP-MS has been, and still is to some extent, a problematic issue. The lack of a commercially available calibration standards forces researchers to develop approaches aimed at particular applications.<sup>2</sup> Since the laser ablation process itself is rather complex due to fractionation and matrix effects, a simple yet reliable calibration method would be appreciated.

Two significantly different calibration approaches are presented. The first is based on laboratory prepared matrix – matched standards which now is already an established approach in the LA-ICP-MS quantitative analyses.<sup>3</sup> In order to test the method for Zn and Mg mapping in rats' hippocampus, standards were prepared with a use of rat brain tissue homogenized, spiked with solutions of selected elements and frozen. After cutting by a microtome, slices were deposited on microscopic glasses and in this form used to build an extrapolative calibration curve. This method is confronted with a second approach using coefficients calculated on a basis of data obtained by conventional solution analysis performed by ICP-MS and by analysis of solid standards by LA-ICP-MS. The coefficients are ratios of average analyte signals measured during ablation and corresponding mean concentration determined in solutions by ICP-MS. Such an approach has been successfully applied for determination of Sr and Ba in historic teeth.<sup>4</sup>

For Zn the coefficient values are very stable with average equals  $0.67 \pm 0.05 [\mu\text{g g}^{-1}]^{-1}$ . In the case of Mg a slight tendency can be observed of decreasing coefficient value with an increased Mg concentration in standards. Nevertheless, the average value for Mg is  $160 \pm 12 [\mu\text{g g}^{-1}]^{-1}$ . Those average coefficients were used to quantify Mg and Zn on the basis of signals recorded during laser ablation of hippocampus region in rats' brains. As a final result, the maps obtained by means of those two approaches are compared.

The method of combining mean concentrations determined by ICP-MS solution analysis with signals recorded during LA-ICP-MS analysis of solids seems to be a straightforward approach which may significantly simplify the calibration step of LA-ICP-MS analyses and hence contribute to increase the applicability of this technique in many areas of research.

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The research was carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund in the framework of the Polish Innovation Economy Operational Program (contract no. POIG.02.01.00-12-023/08).

# *Underwater LIBS Sessions*

## ***Underwater LIBS***

*(Thu. 15<sup>th</sup> of June, h. 9.15-10.45)*

## Chemical reactions in the plasma for quantitative underwater LIBS.

Tetsuo Sakka<sup>\*A</sup>, Atsushi Kawasaki<sup>A</sup>, Takaya Honda<sup>A</sup>, Ayumu Matsumoto<sup>A</sup>, Ken-ichi Amano<sup>A</sup>,  
Naoya Nishi<sup>A</sup>

<sup>A</sup>Department of Energy and Hydrocarbon Chemistry, Kyoto University, Kyoto, Japan

\*sakka.tetsuo.2a@kyoto-u.ac.jp

**ABSTRACT:** Local thermal equilibrium (LTE) of underwater LIBS plasma is assessed, and the atomic densities in the plasma are analyzed with taking chemical reactions into account. We conclude that a rapid temperature decrease, inevitable for underwater plasma, results in the formation of molecules and clusters in the plasma, and hence, the decrease in the amount of free atoms. This effect should be properly considered for the interpretation of underwater LIBS signal for quantitative analysis. Underwater LIBS is an important technique for deep-sea resource exploration and environmental monitoring of lakes and rivers. Also, it can be a convenient in-situ analysis method of solid materials inevitably submerged in water, which we sometimes encounter in industrial processes, such as electroplating, nuclear waste monitoring, etc. In general, an intensity of a certain atomic line is proportional to the corresponding population density. To relate the population density to the atomic density we have to assume thermal equilibrium among the excitation states. Even under local thermal equilibrium (LTE) condition, however, the atomic density in the plasma is not necessarily proportional to the elemental composition of the target material, due to chemical reactions in the plasma which changes the density of free atoms, as well as a possible non-stoichiometric nature of the ablation process. Such disturbance by chemical reactions applies also to underwater LIBS.

In the present work we clarify if LTE condition is attained in the plasma, and investigate the decrease in the density of free atoms due to the formation of diatomic molecules by assuming LTE. We first evaluated the excitation temperatures of Zn and Cu atoms in the plasma, and discuss LTE. The temperature of Zn is close to that of Cu in the plasma in water, suggesting that LTE is probably attained in this system, while they are quite different in air, suggesting that the plasma in air is not in LTE. We have investigated reactions of atoms by nanosecond time-resolved atomic absorption spectroscopy, and obtained absolute amount of the atoms in the ground state, which is the majority among all the populations of possible states of the atom. It was found that the densities of atoms decrease to almost zero after  $\sim 10 \mu\text{s}$ . If we look at the data carefully, Al atoms disappear more rapidly than Na atoms (see Fig. 1). We also calculated the amount of oxide, i.e., AlO and NaO, formed under the equilibrium condition among the related species, by assuming the rate of temperature decrease obtained in our previous work [1]. We conclude that a rapid temperature decrease results in the formation of molecules and clusters in the plasma, and hence, the decrease in the amount of atoms, which should be taken into account for the interpretation of underwater LIBS signal for quantitative analysis.

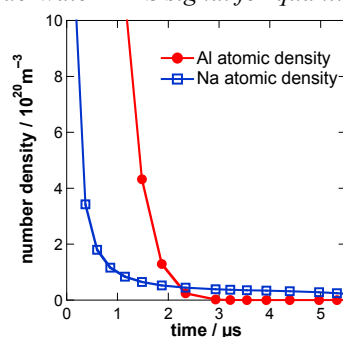


Fig. 1. Calculated number density of Al and Na in the plasma as a function of delay time.

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## Reflections on 5 years of LIBS Deployments for Deep-Sea Research.

B. Thornton<sup>1,2</sup>, T. Takahashi<sup>2</sup>, Tetsuo Sakka<sup>3</sup>

<sup>1</sup>Southampton Marine and Maritime Institute, University of Southampton, Southampton, SO16 7QF, UK,

<sup>2</sup>Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

<sup>3</sup>Kyoto University, Nishikyo-ku Kyoto-shi, Kyoto 615-8510, Japan

\* B.Thornton@soton.ac.uk

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**ABSTRACT:** Our group has been developing LIBS instruments and deploying them in the deep-sea for oceanographic research and mineral prospecting since 2012 [1,2]. Systems have been deployed in 3 different active hydrothermal fields; Wakamiko Caldera (Kagoshima bay), Iheya North Field (Okinawa trough) and Sunrise deposit (Myojin Knoll Caldera) at depths of between 190 and 1300 m. Measurements of both seawater and mineral deposits have been made from work class remotely operated vehicles (ROV) and several 10,000s of analytically useful spectra have been obtained. In this talk we will discuss how the technology has advanced, the lessons that have been learnt and will present the latest data from our most recent expeditions. While the fundamental breakthrough technology has been the development of compact, reliable long-pulse (>100 ns) lasers, we will give particular focus to developments in the operational aspects of deep-sea LIBS instrumentation that now makes measuring seafloor deposits routine. Different methods of analysing LIBS signals [3,4] being investigated by our group will be discussed and we will identify gaps in marine sensing technology that can potentially be filled by LIBS

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## Analysis of underwater long-Pulse LIBS signals using Artificial Neural Networks.

S. Yoshino<sup>\*A</sup>, T. Takahashi<sup>A</sup>, B. Thornton<sup>A,B</sup>

<sup>A</sup>Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan;

<sup>B</sup>Southampton Marine and Maritime Institute, University of Southampton Boldrewood Innovation Campus, Southampton, SO16 7QF, UK

\*soichi@iis.u-tokyo.ac.jp

**ABSTRACT:** This study investigates methods to analyze LIBS signals generated underwater using a long ns-duration pulse (>100 ns) using Artificial Neural Networks (ANNs). Long-pulse LIBS has the unique advantage that signals can be obtained from solid surfaces that are submerged at high, oceanic pressures, and has been applied to in situ geological surveys of deep-sea mineral deposits<sup>1</sup>. While high quality signals can be obtained using this method, the signals are broader and more susceptible to fluctuations than signals in a gaseous atmosphere<sup>2</sup>. Methods to classify and quantify signals generated underwater are still the subject of on-going investigation. Underwater LIBS measurements suffer from increased sensitivity to surface conditions and chemical heterogeneity combined with transient plasma properties and plasma confinement that are specific to underwater measurements. While studies have looked into the use of multivariate techniques<sup>3</sup>, here we will investigate the use of ANNs to describe the non-linear properties. It is generally agreed that for ANNs, pre-processing of full-field data is important and many methods have been proposed in image and language processing fields. Several reports applied ANNs to LIBS in air by choosing elemental peaks to produce results with relatively small training datasets. However, for spectra generated in water, the elemental peaks are not resolved well because the spectra are broad and in some cases self-absorbed due to high plasma density. Therefore, in this work we use the entire signal as input so that these effects can be taken into account rather than manual selecting of specific peaks. This also has the advantage of building a more generic model that can potentially be applied to a broad range of target matrices. At the same time, this also requires larger training datasets and often requires the use of pre-processing and auto-encoding methods for the models to converge. In this study, different approaches to signal preprocessing are assessed.

The LIBS spectra are subject to following steps of pre-processing, in order to suppress fluctuations in intensity due to distance variations to the sample, fluctuations in laser pulse energy and target surface conditions. In addition to these standard steps, averaging of signals is performed to reduce the effect of sample heterogeneity. The effect is bigger in underwater measurements than in air because the incompressibility of water confines the size of plasma. To generate ANN input data, random sampling is performed to generate a larger database, a logarithm of the signals is taken and they are normalized to have a variance of 1 to create a suitable shape for the data. Our study has found that signal pre-processing considering the features of LIBS spectra in water improves classification accuracy from 78.2% to 98.0% for a generic ANNs taking as input, entire LIBS signals with no human specification of features. In our future work, we will apply this method to geological classification of LIBS spectra obtained during in-situ measurements and investigate way to extend this method for quantitative analysis.

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2 R.C. Wiens, et al., Spectrochim. Acta B 82 (2013) 1-27

3 T. Takahashi, et al., Spectrochim. Acta B 124 (2016) 87-93

4 Tensor flow, <https://www.tensorflow.org/>

## Single and Double pulse laser-induced breakdown spectroscopy of solids in water: effect of hydrostatic pressure on laser induced plasma, cavitation bubble and emission spectra.

M. Dell'Aglio\*<sup>A</sup>, M. López-Claros\*<sup>B</sup>, G. Valenza<sup>A, C</sup>, A. Santagata<sup>D</sup>, A. De Giacomo<sup>A, C</sup>, F.J. Fortes<sup>B</sup>, J.J. Laserna<sup>B</sup>

<sup>A</sup> CNR-NANOTEC, Via Amendola 122/D, 70126, Bari, Italy; <sup>B</sup> Department of Analytical Chemistry, Faculty of Sciences, University of Malaga, Campus de Teatinos s/n, 29071, Malaga, Spain; <sup>C</sup> University of Bari, Dipartimento di Chimica, Via Orabona 4, 70125, Bari, Italy; <sup>D</sup> CNR-ISM C.da S. Loja – Zona Industriale, 85050, Tito Scalo, Potenza, Italy.

\*marcella.dellaglio@cnr.it

**ABSTRACT:** A growing interest in the development of technologies for use in exploration of the deep ocean is apparent. Of special relevance are techniques for the chemical analysis of submerged solids, which show promise for subsea mining applications where a rapid sorting of materials found in the sea bottom would improve efficiency. Laser-induced breakdown spectroscopy has demonstrated potential for this application by its unique capability for providing the atomic composition of underwater solids. In this work, the study of the effect of the hydrostatic pressure during the laser ablation of a solid target immersed in water was employed during the single (SP) [1] and double pulses (DP) [2] laser ablation experiments. The main aims were, on one hand, the optimization of the Double collinear LIBS for the underwater applications, on the other hand the connection of the observed plasma parameters with the produced NPs features that concern important applications in material science and that can interfere with the LIBS measurements. The SP and DP laser ablation experiments in water were investigated by Optical Emission Spectroscopy (OES), tempo-rally resolved imaging and shadowgraph techniques, in a range of pressure between 1 to 120 Bar. The temperature and the electron density of the laser induced plasma during the SP experiment have been directly connected with the produced NPs features. The analysis of the plasma behavior and cavitation bubble dynamics put in evidence how, during the SP experiment, although the increasing of the water pressure changes the plasma shaping and aspect ratio, as well as the bubble shape and dynamics, the produced spherical nanoparticles characteristics seems to not be affected by the liquid pressures. The same study on plasma and cavitation bubble was then employed to optimize the DP LIBS experiment in terms of the interpulse delays and NPs interference. It was finally demonstrated that, although the lifetime of the cavitation bubble at high water pressure is too short to obtain the classical advantages of the DP-LIBS at atmospheric conditions, the use of the spectra for elemental analysis with conventional methodologies is still feasible. As a matter of fact, the emission spectra present the emission lines completely absorbed on the continuum radiation due to the initial stage of plasma expansion. These absorbed spectral lines on the continuum have been observed to be proportional to the total number density of the emitting species exhibiting that the state distribution function of the elements holds a Boltzmann form.

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## Quantitative elemental analysis of water-submerged solids using PLS with temperature segmented database for LIBS.

Tomoko Takahashi<sup>\*A</sup>, Blair Thornton<sup>A,B</sup>, Yutaro Takaya<sup>C</sup>, Tatsuo Nozaki<sup>D</sup>, Takumi Sato<sup>A</sup>,  
Toshihiko Ohki<sup>A,E</sup>, Koichi Ohki<sup>E</sup>, Tetsuo Sakka<sup>F</sup>

<sup>A</sup>Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro, Tokyo, Japan; <sup>B</sup>Southampton Marine and Maritime Institute, University of Southampton, Burgess Road, Southampton, UK; <sup>C</sup>School of Creative Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo, Japan; <sup>D</sup>Japan Agency for Marine-Earth Science and Technology, 2-15 Natsushima-cho, Yokosuka, Kanagawa, Japan; <sup>E</sup>OK Lab. Co. Ltd., 8-7-3 Shimorenjyaku, Mitaka, Tokyo, Japan; <sup>F</sup>Department of Energy and Hydrocarbon Chemistry, Kyoto University, Nishikyo-ku, Kyoto, Japan

\* takahas@iis.u-tokyo.ac.jp

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*ABSTRACT: In this study, quantitative elemental analysis of water-submerged metals and rocks is investigated for application to in-situ measurements of deep-sea rocks. In order to reduce effects of shot-to-shot fluctuations seen in signals of water-submerged solids on PLS, database segmentation by excitation temperature is proposed. It was found that segmentation with the appropriate temperature range showed the significant enhancement of the accuracy.*

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# *Fundamentals of Mass Spectrometry Sessions*

## ***MassSpect***

*(Thu. 15<sup>th</sup> of June, h. 11.15-12.30)*

## Advances and future trends in desorption electrospray-mass spectrometry

Maria Careri

Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, University of Parma, Parco Area delle Scienze 17/A Parma, Italy.

maria.careri@unipr.it

**ABSTRACT:** *An outlook on the current status and trends in desorption electrospray-mass spectrometry (DESI-MS), one of the most used spray-based techniques for ambient ionization, is given with an emphasis on applications related to the life sciences, forensics and food analysis. The main advances recently achieved or still in progress regarding studies of the analysis of surfaces affecting the efficiency of the DESI process are discussed<sup>1</sup>. This presentation explores also the move towards recent advancement of DESI-MS that has paved the way for the development of ambient ionization techniques including reactive DESI-MS, electrospray-assisted laser desorption ionization (EALDI) and DESI-MS imaging<sup>2</sup>.*

*Recent technological developments in DESI-MS imaging of biological samples for the detection of drugs and metabolites in tissues, of latent fingerprints in criminal investigations and many other imaging applications attested the potential of this MS technique to analyze spatial localization and molecular distribution of target molecules within a variety of samples, thus providing ambient, label-free imaging with no sample modification. Very recently, a new approach for constant-distance mode mass spectrometry imaging of biological samples using nano-spray desorption electrospray ionization (nano-DESI) was demonstrated to be ideally suited for characterizing biological samples of complex topography in their native states<sup>3</sup>.*

*In the past few years, remarkable advancements in the coupling of liquid chromatography (LC) with MS through a DESI source using ultra-fast LC or ultra-performance (UP) LC have been made. Characteristics include a wide range of elution flow-rates, on-line selective derivatization via reactive DESI, and further combination with electrochemistry (EC) experiments to obtain a UPLC/EC/DESI-MS system, which allows the separated analytes to further undergo redox reactions prior to MS detection. Integration of electrochemistry with UPLC-MS broadens LC/DESI-MS applications such as fast structural elucidation of disulfide-containing proteins/peptides from enzymatic digests, making this innovative technology valuable for proteomics research<sup>4</sup>. The strategy of surface desorption/ionization of analytes from solid-phase microextraction (SPME) for ambient MS led to a number of coupled techniques including SPME/DESI-MS, which have been proved ideal for screening purposes of trace compounds in complex samples for environmental testing, clinical research and forensic analysis<sup>5</sup>. The minimal specimen preparation required for analysis, enhancement of analysis throughput and the sensitivity of detection achieved offer great advantages, especially when coupling DESI with a high-resolution mass spectrometer. However, further improvements particularly in terms of development of novel coating materials for enhancement of both extraction and ionization efficiencies are expected.*

*Finally, future perspectives regarding the implementation of DESI in conjunction with a portable mass spectrometer to develop a robust technique ideal to be used in homeland security and environmental monitoring are discussed.*

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## Certified Reference Materials for Atomic and Molecular Mass Spectrometry

Ewa Bulska\*, Anna Konopka, Anna Łuciuk, Agnieszka Krata, Anna Ruszczyńska, Barbara Wagner, Marcin Wojciechowski

Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, Żwirki i Wigury 101, Warsaw, 02-089, Poland

\*ebulska@chem.uw.edu.pl

*ABSTRACT: The use of certified reference materials (CRM) become highly important, when the quality of the results is consider. In order to calibrate the instrument as well as to assure the traceability of the results, the analyst should select the adequate chemical standard. The common approach for preliminary calibration of given instrument is to use the standard solutions of pure compound of interest. In order to evaluate the influence of the matrix components on the signal and to calculate the experimental recovery, there is a need to select the appropriate reference material, characterized by the close as much as possible, composition in respect of matrix and analyte. Although it is possible to purchase the wide assortment of pure standard compounds, the availability as well as the selection of matrix-matched standards is still recognized as a challenge in respect of assuring the accurate quantitative analysis.*

*The aim of the presentation is to evaluate the selection of the matrix certified reference materials with the purpose of they use in atomic and molecular mass spectrometry, in the case of liquid and solid samples analysis. The special attention will be given to the certification procedure, where GF-AAS, ICPMS, LA-ICPMS or IDMS were used for the determination of the total content of the elements of interest. In some cases, the speciation issue was also consider, for this purpose the use of HPLC-ICPMS was optimize and the operational defined certified value for the species of interest was described. Moreover, various calibration strategies tailored towards specific applications were developed as to assure the accuracy of the results. The evaluation of the advantageous and limitations of the applied CRM as well as calibration modes will be given with the specific examples of environmental samples.*

*In the case of molecular mass spectrometry, the strategy applied for the implementation of the standards for biologically active substances in living organisms will be given with the examples of selected proteins and doping substances. For this purpose the use of LC-MS/MS will be illustrated.*

### Acknowledgements

*Financial support from National Centre of Science (NCN, Poland), project 2013/09/B/ST4/00949, in the years 2014 - 2017, is gratefully acknowledged.*

*The study was carried out at the Biological and Chemical Research Centre, University of Warsaw, established within the project co-financed by European Union from the European Regional Development Fund under the Operational Programme Innovative Economy, 2007 - 2013..*

## Trends in Single Particle and Single Cell ICP-MS Analysis - Significant Instrument Settings and their Implications on Data Quality

Chady Stephan<sup>\*A</sup>, Riccardo Magarini<sup>B</sup>, Marco Buonaguidi<sup>A</sup>

<sup>A</sup>PerkinElmer Canada, 501 Rowntree Dairy Road, Woodbridge, Ontario, Canada;

<sup>B</sup>PerkinElmer Italy, Milan, Italy.

\*chady.stephan@perkinelmer.com

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**ABSTRACT:** During the last decade, the production and use of engineered nanomaterials (ENMs) have experienced a drastic increase, resulting in a potential risk of their release into the environment. Therefore, the study of their impact on the biota becomes crucial. The appropriate ecological risk assessment and management of ENMs in the environment requires quantitative measurements of both exposure and effects that should, ideally, be performed by in situ analysis and give physicochemical characterization. However, most analytical techniques (TEM, SEM, DLS...) are not suitable for environmental matrices since nanoparticle concentrations are very low. Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) has been found to be the technique of choice for detecting and characterizing metal nanoparticles at very low concentrations. SP-ICP-MS is founded on the concept of acquiring fast continuous transient readings offering the ability to distinguish between particles of different elements and the measurement of particle number concentration, particle size, size distribution along with the dissolved concentration for each element. With the key feature of SP-ICP-MS "discrete pulse detection and quantification in a time-resolved manner using microsecond ( $\mu$ s) data acquisition rates" Single Cell ICP-MS (SC-ICP-MS) is introduced, where individual cells are analyzed for metal content at the individual level.

This work will focus on the various significant instrument settings and their implications on nanoparticle and single cell characterization. Information on the instrument setup conditions and the influence of transport efficiency on data quality is given. The effect of varying the dwell time and its influence on particle integration, particle counting, particle sizing, and the background signal is discussed. Data describing the use of Dynamic Reaction Cell (DRC) design in handling short-lived transient events while managing spectral interferences is also discussed.

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*Nano-LIBS Sessions*

***NanoLibs***

*(Thu. 15<sup>th</sup> of June, h. 14.15-16.30)*

## Perspectives of Nanoparticle Enhanced Laser Induced Breakdown: the laser matter interaction under NPs control

Can Koral<sup>A</sup>, Rim Alrifai<sup>A</sup>, Gabriele Valenza<sup>A</sup>, Rosalba Gaudiuso<sup>B</sup>, Marcella Dell'Aglio<sup>B</sup>, Alessandro De Giacomo<sup>A,B\*</sup>

<sup>A</sup>Department of Chemistry, University of Bari, Via Orabona 4, 70125 Bari-Italy; <sup>B</sup>CNR-NANOTEC, Via Orabona 4, 70125 Bari Italy.

\* alessandro.degiacomo@nanotec.cnr.it

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*ABSTRACT: In 2013 we proposed the Nanoparticle Enhanced Laser Induced Breakdown Spectroscopy (NELIBS) for enhancing the LIBS performances in terms of signal enhancement in several applications, spacing from metal sample analysis to biological samples [1]. After a few years several groups around the world have applied NELIBS in different applications. Although the promising results presented by several authors, the basic concepts of the laser matter interaction when NPs are deposited on the sample are still receiving poor consideration leading to misunderstand the real advantages and the limitation of this powerful technique. In this view this lecture is devoted to discuss the basic aspects of NPs supported laser ablation and overview the critical points in sample preparation for NELIBS. Finally a general overview of the future perspectives and applications of NELIBS will be critically discussed in order to outline the advantages and the limitation of this recent technique.*

*References: De Giacomo, A., Dell'Aglio, M., Gaudiuso, R., Koral, C., Valenza, G. Perspective on the use of nanoparticles to improve LIBS analytical performance: Nanoparticle enhanced laser induced breakdown spectroscopy (NELIBS) (2016) Journal of Analytical Atomic Spectrometry, 31 (8), pp. 1566-1573.*

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## Laser-induced nanoparticle formation and its application for LIBS enhancement

C. Sánchez-Aké<sup>\*A</sup>, T. García-Fernández<sup>B</sup>, M. Villagrán-Muniz<sup>A</sup>, F. Bredice<sup>C</sup>, B. de la Mora<sup>D</sup>, J.L. Benítez<sup>A</sup>, R. Castañeda-Guzmán<sup>A</sup>

<sup>A</sup>Laboratorio de Fotofísica, Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México, Apartado Postal 70-186, México D.F., C.P. 04510, México; <sup>B</sup>Universidad Autónoma de la Ciudad de México (UACM), Prolongación San Isidro 151, San Lorenzo Tezonco, México D.F., C.P. 09790, México;

<sup>C</sup>Centro de Investigaciones Ópticas (CIOp), C.C.3, 1897, Gonnet, La Plata, Argentina; <sup>D</sup>CONACyT Research Fellow- CCADET, Universidad Nacional Autónoma de México (UNAM), México D.F., 04510, México.

\*citlali.sanchez@ccadet.unam.mx

**ABSTRACT:** We investigate the features of Au metal nanoparticles (NPs) formation by laser irradiation of thin films and its application in Nanoparticle Enhancement Laser Induced Breakdown Spectroscopy (NELIBS). In this approach, the formation/modification of NPs and the enhancement of the LIBS signal are produced simultaneously by a single laser shot. The NPs are formed by nanosecond laser exposure of Au thin films previously deposited on transparent dielectric substrates. The irradiation induces phase changes resulting in the formation of metallic nanoparticles (NPs) attached or even embedded in the surface of the substrate[1,2]. Those NPs enable the enhancement of the LIBS signal allowing the analysis of glasses at much lower irradiance than in conventional LIBS[3]. Experiments of irradiation of Au thin films were carried out for studying the formation of NPs, which revealed the fundamental role of the metal/substrate evaporation and plasma formation in the produced nanostructures and in their corresponding optical properties. The influence of the starting film thickness, laser fluence and number of pulses on both, the characteristics of the NPs and the enhancement of the emission signal was also studied. The obtained NPs were characterized by SEM and UV-Vis optical absorption. It has been found that for low fluences, the NPs are formed on the surface of the substrate allowing the increasing of the LIBS signal for few pulses. In contrast, for high laser fluences the NPs are implanted into the substrate allowing the emission enhancement for hundreds of pulses.

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## Nano-sampling of metals with ultra-short laser pulses

Alexandre Semerok <sup>\*A</sup>, Sergey V. Fomichev <sup>B, C</sup>

<sup>A</sup> DEN-Service d'Etudes Analytiques et de Réactivité des Surfaces, CEA, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France; <sup>B</sup> National Research Center "Kurchatov Institute", 123182 Moscow, Russia; <sup>C</sup> Moscow Institute of Physics and Technology, 141700 Dolgoprudny, Moscow region, Russia.

\*alexandre.semerok@cea.fr

**ABSTRACT:** In sample microanalysis by laser ablation (LA), spatial resolution is determined by laser beam diffraction limits (of the order of a laser wavelength) and thermal diffusion of a deposited heating energy during laser pulse (proportional to the square root of pulse duration and matter diffusivity). Being limited by these laser beam features and those of heating energy, spatial resolution (a crater diameter) of  $\sim 1 \mu\text{m}$  was obtained with 4 ns laser pulses on 266 nm wavelength <sup>1-2</sup>. To improve spatial resolution of microanalysis, the application of lasers with the pulses of shorter durations (ps and fs) may be advised <sup>3-5</sup>. As another way to improve spatial resolution of microanalysis up to  $\sim 100 \text{ nm}$ , one may advise LA with a highly localized laser field created by a tip near-field enhancement <sup>6</sup>. The experiments with ns laser pulses were made along with multi-parametric theoretical studies <sup>7</sup> based on one-temperature heating model.

In this work, the theoretical studies were extended on ultra-short laser pulses (ps or fs) to analyze the effect of pulse duration and matter properties (absorption coefficient, thermal conductivity and capacity) on the resulting temperature field spatial distribution  $T(t, x, y, z)$ . A two-temperature model was applied for  $T(t, x, y, z)$  calculations. The results of these simulations are compared to temperature distributions for ns laser pulses. Discussion on advantages of ultra-short pulses application for LA with a tip near-field enhancement for consecutive chemical analysis with nanometric resolution will be presented.

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## Green Synthesis of Silver Nanoparticles and Their Application in the Laser Induced Breakdown Spectroscopy Technique

B. Campanella<sup>A</sup>, E. Grifoni<sup>A</sup>, S. Legnaioli<sup>A</sup>, G. Lorenzetti<sup>A</sup>, S. Pagnotta<sup>A</sup>, V. Palleschi<sup>A</sup>, F. Poggialini<sup>A\*</sup>

<sup>A</sup> Applied and Laser Spectroscopy Laboratory, Institute of Chemistry of Organometallic Compounds, Research Area of CNR, Via Giuseppe Moruzzi, 1, 56124 Pisa (Italy)

\*francesco.poggialini@gmail.com

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*ABSTRACT: When compared to other analytical techniques such as XRF, ICP-OES/MS and AAS, LIBS shows relatively low precision and, generally, high LODs. Traditionally, the enhancement of LIBS performances is based on the introduction of more powerful lasers, high sensitivity detectors or controlled environmental parameters. This can hinder the competitiveness of LIBS by increasing the instrumental setup cost and the difficulty of operation. Sample treatment has proved to be a viable and simple way to increase the LIBS signal; in particular, the NELIBS methodology uses a deposition of metal nanoparticles on the sample to greatly increase the emission of the LIBS plasma. In this work, we used a simple, fast, “green” and low-cost method to synthesize silver nanoparticles by using coffee extracts as a reducing agent for a silver nitrate solution. This allowed us to obtain nanoparticles of about 25 nm. We then explored the application of such nanoparticles to the NELIBS analysis of metallic samples with a proprietary portable LIBS instrument (Modi). By adjusting the laser parameters and optimizing the sample preparation procedure, we obtained a signal enhancement throughout the study. This showed the potential of green-synthesized nanoparticle for NE-LIBS applications.*

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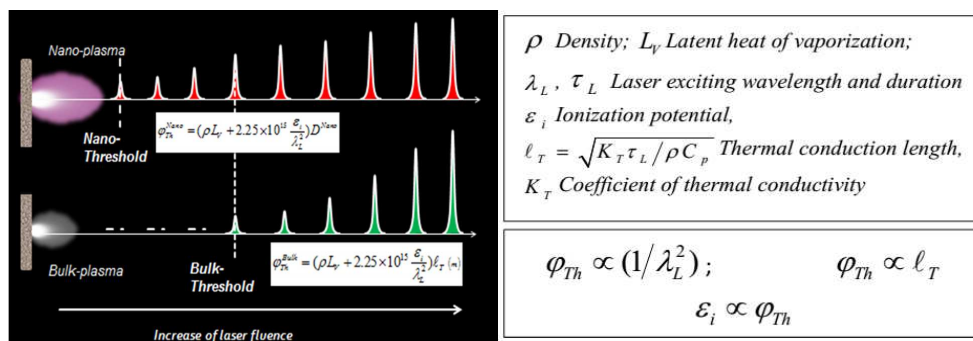
## On nanoparticle enhanced laser-induced emission spectroscopy

Ashraf M. EL Sherbini<sup>\*A</sup>, Fatimah. H. Alkallas<sup>B</sup>, Christian G Parigger<sup>C</sup>

<sup>A</sup> Department of Physics, Cairo University, Faculty of Science, Lab. of lasers and New Materials, Giza, Egypt; <sup>B</sup> Physics Department, Laser lab, Princess Nora University, Riyadh, Saudi Arabia; <sup>C</sup> Department of Physics and Astronomy, University of Tennessee, University of Tennessee Space Institute, Center for Laser Applications, 411 B.H. Goethert Parkway, Tullahoma, TN 37388, U.S.A.

\*elsherbinia@sci.cu.edu.eg

**ABSTRACT:** Enhanced emission was observed from plasmas induced by focusing nanosecond pulsed laser radiation on nano-matter distributions. These studies include experiments utilizing pure nanoparticles [1-4] and the use of thin layer metallic nanomaterials to cover solid targets [5-7]. The acronyms for nanomaterial enhanced laser-induced plasma spectroscopy (NELIPS) and nanomaterial enhanced laser-induced breakdown spectroscopy (NELIBS) appear to be used freely to annotate the increase in signal yield. Figure 1 illustrates signal enhancements achieved in experiments together with efforts in modeling.



**Figure 1: Nano-material signal enhancement and modeling summary.**

In this work, the different approaches and outcomes are discussed. When using pure nanoparticles (termed NELIPS by some researchers), the measurements of principle plasma parameters are accomplished using traditional plasma spectroscopy [1-4]. The recorded signals show (a) increase linearly with time delay, (b) scales logarithmically with reduction of the laser fluence, (c) shows similar plasma parameters, (d) are compatible with the relative concentrations from bulk and nano-material, (e) reduce plasma threshold fluence for excitation wavelengths towards the UV, and (f) reduce the threshold upon decreasing nanoparticle sizes suggesting the scaling of classical thermal conduction length to the nanomaterial diameter. When using thin layer of nanoparticles on surface of sample targets (termed NELIBS by some researchers), enhanced signals from the target material has reported for several base materials [5-7], effectively increases the limit-of-detection figure of merit. For pure nanomaterial, it could be of interest to elucidate the role of laser-plasma thresholds for modeling of measured enhancements.

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## Development of a New Method for Structural Analysis Of Ge Nanoparticles Embedded ZnO Thin Films By Laser Induced Breakdown Spectroscopy

Kemal Efe Eseller<sup>\*A</sup>, M. Sinan Topcu<sup>B</sup>, Abdullah Ceylan<sup>B</sup>, Banu Sezer<sup>C</sup>, Gonca Bilge<sup>C</sup>, Ismail H. Boyacı<sup>C</sup>

<sup>A</sup> Electrical and Electronics Engineering Department, Atilim University, Ankara, Turkey; <sup>B</sup> Department of Physics Engineering, Hacettepe University, Ankara, Turkey; <sup>C</sup> Department of Food Engineering, Hacettepe University, Ankara, Turkey.

\*efe.eseller@atilim.edu.tr

**ABSTRACT:** Laser Induced Breakdown Spectroscopy (LIBS) has been applied for the large scale structural investigation of nanocomposite multilayered thin film samples. In order to determine the applicability and capability of LIBS on Ge nanoparticles (Ge-np) embedded multilayered ZnO thin films (total thickness~ 900 nm) a new model system has been thoroughly built and compared by other structural analysis techniques such as XRD, SEM, and SIMS. ZnO: Ge thin films were deposited on Si (111) substrates by sequential sputtering of ZnO (~150 nm) and Ge (~30 nm) layers and formation of Ge-np were accomplished by post-deposition rapid thermal annealing (RTA). Energy difference between direct and indirect band transitions for (Ge) is about 0.12 eV which makes it more suitable for changing the electronic structure around band edge. Studies show that Ge nanoparticle embedded oxide materials have significantly changed optical behaviors which is related to the quantum confinement of electron hole pairs in Ge nanoparticles. The structure of Ge nanoparticles and the nature of the interface between oxide material matrix must be understood to interpret this behavior change. Because of quantum confinement effect in Ge atom in less than 24nm Bohr radius particles, transition between two levels are limited energy levels. Ge layer and Ge nanoparticles have a positive effect in ZnO based solar cells efficiency. Most of the studies are done by Si and Ge nanoparticle embedded in wide bandgap semiconducting oxide matrices. Indirect bandgap created with both Si and Ge leads to a longer life time of electron-hole pairs as compared to direct band gap materials. Based on the theoretical studies, Ge is predicted to show a significant quantum confinement effect below 24nm Bohr radius. This limit is much above that of Si which is approximately 5 nm Bohr radius. Hence, it is important to investigate the ZnO:Ge thin films. In order to realize 2D homogeneity of the samples, LIBS measurements have been performed on equally spaced 5 spots of a line matrix. In addition, measurements were repeated on each spot by performing consecutive laser shots so as to obtain depth profiles of the samples. It has been realized that although 2D homogeneity of the samples in terms of the distribution of Zn and Ge atoms could be very well obtained by LIBS, depth profiling is not that reliable due to each laser shot ablating approximately 125 nm with 11.2 mJ pulse energy which was the minimum for observing Ge peaks within an acceptable error margin. For this purpose, LIBS system was developed with maximum spectrum intensity versus sampling methods. Structure of ZnO: Ge samples was identified in less than 1 minute under ambient conditions. Results were compared with SEM and XRD results. Discrimination analysis (principle component analysis, PCA) have been performed to investigate different thin film structures. Eventually, signal to noise (SNR) and signal to background (SBR) ratios of elements have been evaluated to maintain the best detection conditions.

## Attogram sensitivity through laser-induced breakdown spectroscopy of single optically-trapped nanoparticles

Pablo Purohit\* and Javier J. Laserna

<sup>A</sup>Department of Analytical Chemistry, University of Málaga, Campus de Teatinos s/n 29070 Málaga, Spain

\*purohit@uma.es

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**ABSTRACT:** Current trends in nanoengineering are bringing along new structures for usage over a wide variety of fields: from readily available products, e.g., clothes or foodstuff, to next-generation electronics or drugs. To suit their corresponding application, nanodevices feature increasingly complex chemical compositions, which need to be meticulously defined even at single particle scale to ensure their correct operation as well as to evaluate their potential toxicity. The complete characterization of such exiguous sample quantities demands a great degree of sensitivity met only by few techniques that present drawbacks related to difficult nanoparticles isolation and discrimination of individual-particle events. Thanks to its versatility, laser-induced breakdown spectroscopy (LIBS) offers straightforward simultaneous identification of virtually any kind of sample, hence making it an appealing candidate for single particle analysis, but it is usually hindered by high detection limits. In the present communication, the sensitivity boundaries of LIBS are pushed towards a new extreme as we demonstrate direct attogram detection and identification by combining LIBS and optical trapping (OT). In this approach, individual nano-particles are suspended in an optical trap set in air and subsequently probed. Metallic Cu nanoparticles of diameters comprised between 25 and 70 nm, with masses ranging from 0.073 to 1.61 fg, were steadily trapped under said conditions for the first time. Optical forces acting on the particles were calculated for each sample to assess the stiffness of the trap. A simple classification scheme was developed to discern single Cu particle LIBS events, whose intensities showed linear correlation with particle masses. OT-LIBS showcases a limit of detection of 31 ag for Cu (the mass of a 19 nm particle), unprecedented in optical emission spectroscopy. This sensitivity was linked to more efficient particle dissociation and excitation of smaller size particles in the laser-induced plasma by quantitatively estimating the production of photons per mass unit from recorded spectra. The results described herein should pave the path of LIBS towards the inspection of individual complex nanostructures to the extent of discriminating the presence of undesired trace elements.

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*Computational Spectroscopy Sessions*  
***CompChem***

(Thu. 15<sup>th</sup> of June, h. 14.15-16.30)



## The Virtual Multifrequency Spectrometer: status and perspectives of an undergoing project.

Vincenzo Barone\*

Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy

\*vincenzo.barone@sns.it

*ABSTRACT: The impressive advances of computer power, effective and user friendly software and graphical interfaces are leading to the development of a new generation of virtual tools able to deal effectively with the complex systems and phenomena of current interest in the study of molecular systems. Going from collections of numbers for oversimplified models toward vis-a-vis comparison between in silico and in vitro outcomes for real systems together with 3D renderings and natural interfaces should finally overcome the diffidence of experimentalists versus theoreticians mentioned in the title. Among those virtual instruments, we will be concerned here with the multifrequency spectrometer (VMS) our group is developing in the last few years in the framework of the ERC Advanced Grant DREAMS: 320951 ("Development of a Research Environment for Advanced Modeling of Soft Matter") [1], which allows vis-a-vis comparison of experimental spectra with their simulated counterparts and interpretation of the results in terms of the interplay among different well defined effects [2,3]. The main building blocks of this tool are, apart from powerful 3D pre- and post-processing tools, first-principle and semiempirical [4] models based on the density functional theory for the proper treatment of stereo-electronic effects, polarizable atomistic [5] and continuum [6] models to deal with environmental effects, and perturbative treatments for describing nuclear motions either beyond the harmonic level [7], or involving more than one electronic state [8]. In this presentation I will sketch the present status of the multifrequency spectrometer and the ongoing efforts toward increasing its range of application with special reference to excited electronic states of molecular systems both in the gas phase and in more complex environments. Some case studies will be selected to better illustrate the above concepts.*

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## Quantum Chemical Interpretation of Spectral Properties of Organometallic Complexes in Ground, Excited and Different Redox States.

Stanislav Zális<sup>\*A</sup>, Martin Pižl<sup>A,B</sup>, Antonín Vlček Jr.<sup>A,C</sup>

<sup>A</sup>J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic; <sup>B</sup>Department of Inorganic Chemistry, University of Chemistry and Technology, Prague 6, Technická 5, 166 28, Czech Republic; <sup>C</sup>School of Biological and Chemical Sciences, Queen Mary University of London, UK

\*stanislav.zalis@jh-inst.cas.cz

**ABSTRACT:** Density functional methods (DFT) were used for interpretation of IR, time-resolved IR, absorption and emission spectroscopy experiments. Calculated IR and time-resolved IR spectra were calculated by vibrational analysis at optimized ground- and excited-state geometries using harmonic or anharmonic approaches. The simulation of absorption and emission spectra was based on time-dependent DFT (TD-DFT) methodology. The solvent effects were described by the polarizable continuum model (PCM) or conductor-like screening model (COSMO). The computational procedures describing ground and excited state spectral properties will be illustrated on Re carbonyl diimine complexes  $[\text{Re}(X)(\text{CO})_3(\text{L})]^n$  ( $X = \text{Cl}, \text{Br}, \text{I}, \text{im}, \text{py}$ , protein chain;  $\text{L} = \text{bpy}$  (2,2'-bipyridine) or phen (phenantroline) and dinuclear Pt and Ir systems  $[\text{Pt}_2(\text{BF}_2\text{POP})_4]^{4+}$  and  $[\text{Ir}_2(1,8\text{-diisocyanomenthane})_4]^{2+}$ . Computational results on Re and Pt complexes were successfully compared with spectra measured in different solvents and it was shown that calculations qualitatively explain the temperature-dependence of the phosphorescence decay parameters that were measured for the whole series of Re complexes. Spin-orbit SO-TD-DFT calculated spectra well interpreted experimental UV-vis spectra including the lowest lying singlet – triplet excitations. SO calculations shown the splitting of the lowest triplet states and help to understand photophysical properties. The interpretation of spectroelectrochemical behavior will be illustrated on the redox series of above mentioned Pt and Ir complexes and redox series of Co and Cu complexes with bidentate ligands. TD-DFT reasonably reproduces the experimentally observed spectra variation in the course of redox changes. The proper choice of lowest energy configuration for individual redox states will be emphasized.

## Accessible accurate simulation of vibrational and electronic spectra of medium-to-large molecular systems: the virtual spectrometer

Julien Bloino<sup>A</sup>, Alberto Baiardi<sup>\*B</sup>, Vincenzo Barone<sup>B</sup>

<sup>A</sup> Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti OrganoMetallici (ICCOM-CNR), UOS di Pisa, Area della Ricerca CNR, Via G. Moruzzi 1, 56124 Pisa, Italy, <sup>B</sup> Scuola Normale Superiore of Pisa, Piazza dei Cavalieri 7, 56126 Pisa, Italy.

\*alberto.baiardi@sns.it

**ABSTRACT:** Ongoing work has been dedicated in our group to develop a multi-frequency virtual spectrometer able to simulate a large range of spectra for molecules of biological and technological interest with account for environmental effects[1,2]. A primary objective is to offer accurate results in a cost-effective way while being accessible to a broad community of researchers interested in computational spectroscopy. The platform has been designed in a modular way to facilitate its development and extension. In particular, two modules have been actively built up over the last years. The first one[3-5] aims at simulating vibrational spectra beyond the harmonic approximation, using second-order perturbation level of theory (VPT2) to compute both transition energies and intensities. The second module[6--8] adds vibrational contributions to electronic spectra.

In this presentation, we will describe the main features of the virtual spectrometer and the theoretical frameworks used for the simulation of vibration and vibronic spectra. The simplicity of use of the tool is strongly conditioned by its capability to identify and possibly overcome the shortcoming in the approximations adopted by the basic models on which it relies. The potential impact of such issues, like resonances in VPT2 calculations or molecular deformations and mode mixing upon electronic transition, and strategies to ensure the reliability and accuracy of the results will be discussed. Some capabilities of the spectrometer will be illustrated by several case studies covering various spectroscopies, including chiral effects, and experimental conditions, like mixtures, environment or temperature.

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# Mapping Atomic Orbitals with the Transmission Electron Microscope: Images of Defective Graphene Predicted from First-Principles Theory

Lorenzo Pardini<sup>\*A</sup>, Stefan Löffler<sup>B,C</sup>, Giulio Biddau<sup>A</sup>, Ralf Hambach<sup>D</sup>, Ute Kaiser<sup>D</sup>, Claudia Draxl<sup>A,E</sup>, and Peter Schattschneider<sup>B,C</sup>

<sup>A</sup>Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany, <sup>B</sup>Institute of Solid State Physics, Vienna University of Technology, Austria, <sup>C</sup>University Service Centre for Transmission Electron Microscopy, Vienna University of Technology, Austria, <sup>D</sup>Central Facility for Electron Microscopy, University of Ulm, Germany, <sup>E</sup>European Theoretical Spectroscopy Facility (ETSF)

\*[pardini@physik.hu-berlin.de](mailto:pardini@physik.hu-berlin.de)

**ABSTRACT:** The possibility of mapping atomic orbitals by using an energy-filtered transmission electron microscope (EFTEM) has been considered for a long time and was recently demonstrated from a theoretical point of view [1]. With the example of graphene, we predict how this approach can be used to map orbitals of a particular character [2]. To this extent, we have investigated graphene with two different kinds of defects, namely an isolated vacancy and a substitutional nitrogen atom. We show that basically three different kinds of images are to be expected, depending on the orbital character as determined from the corresponding projected density of states. To judge the feasibility of mapping such orbitals in a real microscope, we investigate the effect of the optics' aberrations, by simulating the lens system of two microscopes that are commonly used for electron energy loss spectrometry. We find that it should indeed be feasible to see atomic orbitals in a state-of-the-art EFTEM.

All the calculations performed in this work can be freely downloaded from the NOMAD Repository [3], which is a repository that was established to host, organize, and share computed materials data. It is part of the NOMAD Laboratory [4], a European Centre of Excellence for Computing Applications.

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## Modeling amide I infrared spectra of proteins: insights from a perturbative approach

Laura Zanetti-Polzi<sup>\*A</sup>, Isabella Daidone<sup>A</sup>, Andrea Amadei<sup>B</sup>

<sup>A</sup>Department of Physical and Chemical Sciences, University of L'Aquila, Via Vetoio (Coppito1), 67010, L'Aquila, Italy; <sup>B</sup>Department of Chemical and Technological Sciences, University of Rome "Tor Vergata", Via della Ricerca Scientifica, 00185, Rome, Italy.

\*laura.zanettipolzi@univaq.it

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**ABSTRACT:** Infrared (IR) absorption spectra of amide modes (particularly of the amide I mode, mostly corresponding to the peptide-group C=O stretching) have long provided a tool for determining the secondary structure of peptides and proteins. Indeed, the amide I band is sensitive to the protein secondary structural components: the frequencies of the amide I band are closely correlated to the molecular geometry and hydrogen bonding pattern. However, the link of particular frequencies with secondary structure has been made on the basis of semiempirical rules and is often controversial. Moreover, the observed amide I bands are often featureless, due to the extensive overlap of the broad underlying component bands. Theoretical-computational methods are needed to provide essential information on the complex relationship between spectroscopic absorption and dynamics, permitting the effects of structural transitions and of solvent interactions on the IR signal to be unravelled. In this context, we proposed and applied an approach to calculate amide I IR spectra of peptides and proteins based on the joint use of extended molecular dynamics (MD) simulations and a mixed quantum/classical theoretical computational methodology: the Perturbed Matrix Method (PMM)[1,2]. In PMM a portion of the system (the quantum center) is treated at an electronic level, while the rest of the system is described at a classical atomistic level, exerting an electrostatic perturbation on the quantum-center electronic states. As the method makes use of classical MD to provide phase space sampling, statistically relevant sampling of the quantum-center/environment configurations can be achieved, which is required for an accurate calculation of the spectra of complex systems. The use of such an approach allowed the theoretical investigation of the amide I spectra of both helical [3,4] and  $\beta$  [1,4-6] peptides as well as amyloids [7] and peptides unfolded states [1,4,6], critically comparing the calculated spectra with experimental IR temperature-dependent and isotope-labelled spectra and providing a mean for the interpretation of the experimental spectra at the molecular level. More recently, we focused on modelling the time-dependence of the amide I IR signal, to be compared with experimental time-resolved IR spectra, commonly used to monitor folding kinetics [6]. The possibility of quantitatively modelling time resolved spectra can provide a detailed interpretation of the time evolution of the spectroscopic signal, permitting a full characterization of the kinetics of complex chemical-biochemical processes. The investigation of time-dependent IR signals is being currently applied to the analysis of extremely long (hundreds of microseconds) folding trajectories of a  $\beta$  peptide, allowing to reconstruct the IR spectroscopic signal of various conformational states of the peptide and providing a thorough thermodynamic and kinetic picture of the folding process. **References:** [1] Daidone, I. et al., Chem. Phys. Lett., 488(4), 213-218, 2010. [2] Amadei, A. et al., Theor. Chem. Acc., 129(1), 31-43, 2011. [3] Zanetti-Polzi, L. et al, J. Phys. Chem. B, 117(41), 12383-12390, 2013. [4] Zanetti-Polzi, L. et al., J. Phys. Chem. B, 116(10), 3353-3360, 2012. [5] Zanetti-Polzi, L. et al., J. Phys. Chem. B, 115(41), 11872-11878, 2011. [6] Daidone, I. et al., J. Phys. Chem. B, 119(14), 4849-4856, 2015. [7] Zanetti-Polzi, L. et al., J. Am. Chem. Soc., 133(30), 11414-11417, 2011

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## High accuracy simulation of XRF spectra of transition metals.

Mauro Guerra<sup>\*A</sup>, Jorge M. Sampaio<sup>B,C</sup>, Fernando Parente<sup>A,C</sup>, José P. Marques<sup>C</sup>, Paul Indelicato<sup>D</sup> and José Paulo Santos<sup>A</sup>

<sup>A</sup> Laboratório de Instrumentação, Engenharia Biomédica e Física da Radiação (LIBPhys-UNL), Departamento de Física, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, Monte da Caparica, 2892-516 Caparica, Portugal; <sup>B</sup> LIP – Laboratório de Instrumentação e Física Experimental de Partículas, Av. Elias Garcia 141D, 1000-149 Lisboa, Portugal; <sup>C</sup> BioISI – Biosystems & Integrative Sciences Institute, Faculdade de Ciências da Universidade de Lisboa, Campo Grande, C8, 1749-016 Lisboa, Portugal; <sup>D</sup> Laboratoire Kastler Brossel, UPMC-Sorbonne Universités, CNRS, ENS-PSL Research University, Collège de France, France

\*mguerra@fct.unl.pt

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*ABSTRACT: High-resolution X-ray spectroscopy has revealed complex structures in the spectra of core-ionized elements essentially due to the interaction of the inner unpaired electron with the atom's valence electrons. In this way, the transition metals are well suited study objects due to their open 3d shell. To this date, the analysis of experimental spectra requires multi peak fitting including up to 12 or more parameters depending on the complexity of the system and whether satellite lines are present. These parameters include not only experimental features such as spectrometer energy resolution and transfer functions but also energy shifts, natural transition widths, spectator intensities and broadening. In this work, we have performed simulations of high accuracy X-ray spectra of selected transition metals, using a completely ab initio technique where all of the radiative and non-radiative transitions were calculated with the Dirac-Fock method including the Breit operator and quantum electrodynamic corrections such as self-energy and vacuum polarization. The simulation of the spectra is then free of any fitting parameters, requiring only as input the experimental energy resolution, background intensity and any energy offset due to calibration procedures. Noteworthy is the fact that the ratio between the diagram and the satellite lines intensities is not subject to any fitting, being obtained directly from their calculated relative intensities. We have also investigated the influence of low energy configurations, besides the ground state configuration, in the simulated spectra, as they can be populated at the temperature at which the experiment is run. Comparison with experimental spectra from different compounds of the studied metals was also performed in order to investigate the chemical shifts and other solid-state effects.*

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## Computational modelling of chiroptical properties of transition metal complexes

Marco Fusè<sup>\*A</sup>, Alberto Baiardi<sup>A</sup>, Vincenzo Barone<sup>A</sup>, Julien Bloino<sup>B</sup>

<sup>A</sup>Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy

<sup>B</sup>National Research Council of Italy, Institute of Chemistry of Organometallic Compounds, Via G. Moruzzi 1, 56124 Pisa, Italy

\* marco.fuse@sns.it

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**ABSTRACT:** *In recent years, enantiopure metal complexes have attracted growing interest for their possible application in several fields such as catalysis, materials and life science.[1,2] Molecular properties are commonly studied through spectroscopic methodologies, which can be combined to get a complete description of the systems. Among them, chiroptical methodologies are the fundamental experimental techniques to assess the molecular chirality, and have been widely applied to determine the absolute configuration of chiral molecules. However chiroptical experimental spectra can be only seldom interpreted on a basis of classical or phenomenological models.[3] This is particularly true for transition metal complexes, where the chiroptical activity arises from many different contributions. For those systems, only accurate theoretical models allow a complete understanding of the information present in an experimental spectrum. In medium-to-large systems (more than twenty atoms), such as most organometallic ones, very accurate calculations are not feasible due to the computational cost. Thus, the best methodology for the systems should be carefully chosen on the base of the dimension and topology of the systems. A balance between the needs for reasonable computational costs and accuracy can be achieved on several aspects, like the electronic structure calculation methods or the model used for the simulation of the spectra. For the former, for instance, a tailored multilevel schemes can be designed, such as only some of the needed quantities are computed at a high-level of theory. Regarding the latter, in literature, electronic spectra calculations are still mainly based on approximated approaches, where broadening effects are usually added to electronic spectra using symmetric broadening functions, such as Gaussian or Lorentzian distribution functions. However, all electronic spectra band-shapes are the result of the convolution of vibronic transitions, giving in general highly asymmetric band-shapes, both in low and in high-resolution spectra.[4] This aspect is even more critical for chiroptical spectroscopies (such as electronic circular dichroism ECD and circularly polarized luminescence CPL) due to their high sensitivity and the possibility of sign changes.[5,6] Consequently, a reliable simulation of the electronic spectra should take into account the effects of the molecular vibrations. Here, we present some experimental and computational results about the electronic chiral spectroscopic properties of transition metal complexes (ECD and CPL), for which different vibronic models have been tested.*

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*Nuclear Applications Sessions*  
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## Evaluation of corrosion on materials at the Y-12 Nuclear Security Complex using Hand-Held Laser-Induced Breakdown Spectroscopy

Madhavi Martin<sup>\*A</sup>, Brittany Bennett<sup>B</sup>, Elena Garlea<sup>B</sup>

<sup>A</sup> Oak Ridge National Laboratory, Oak Ridge, TN, USA;

<sup>B</sup> Y-12 Nuclear Security Complex, Oak Ridge, TN, USA;

\*martinm1@ornl.gov

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*ABSTRACT: The focus of this fundamental research is to examine and determine corrosion on nuclear materials present at the Y-12 Nuclear Security Complex site. This has been determined by identification of elements such as hydrogen and oxygen on the material surface using a hand-held laser-induced breakdown spectroscopy (LIBS) instrument. The hand held LIBS instrument was obtained from the company SciApps and the model SciApps Z500 was used to obtain the data that is shown in this presentation. This instrument has a unique software. The excitation laser is an Nd-YAG solid state laser which is operated at the fundamental frequency of 1532 nm. The output energy per pulse is 5mJ. Initially commercially available alloys used as reference samples were tested with using the hand-held instrument. This was used to determine calibration curves for each of the major element that was present in the reference alloy. Materials of interest such as Uranium metal, uranium hydride (UH<sub>3</sub>), and Uranium Oxides (U<sub>3</sub>O<sub>8</sub> and UO<sub>2</sub>) were tested in a glove box in order to identify the constituents related to corrosion within the materials such as the presence of elements such as hydrogen and oxygen. In summary, calibration curves of alloys will be presented and real radioactive specimens LIBS data will be shown. The objectives of using this hand-held LIBS technology is 1) to demonstrate the viability of this technique for a variety of nuclear materials identification and inventory, and 2) to use this information to fingerprint the presence of elements (hydrogen and oxygen) related to corrosion within materials.*

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## Twenty Years of LIBS at Oak Ridge National Laboratory: Nuclear Applications and Future Promise

R. C. Martin<sup>A</sup>, M. Z. Martin<sup>B</sup>, and J. H. Miller<sup>A</sup>

<sup>A</sup> Fusion & Materials for Nuclear Systems Division

<sup>B</sup> Biosciences Division

Oak Ridge National Laboratory  
Oak Ridge, Tennessee, United States

\*martinrc@ornl.gov

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*ABSTRACT: After the ground-breaking work on LIBS by Los Alamos National Laboratory in the 1980s, Oak Ridge National Laboratory (ORNL) became the second nuclear laboratory in the United States to promote LIBS as a versatile analytical tool for nuclear applications. Although ORNL's applications of LIBS to environmental problems is more widely published, several demonstrations of LIBS for nuclear-specific applications have been conducted at ORNL over the past 20 years. This ORNL experience will be reviewed including unpublished data on a high-level radiochemical process solution, a customized low-power laser scribe system installed in a glove box, and laboratory analyses of nuclear fuel and related materials using sealed sample cells. Potential applications of LIBS as a "faster and cheaper" analytical tool to a range of challenging nuclear-related applications will be discussed, along with the practical challenges of working in highly regulated nuclear laboratories.*

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## Development of a LIBS system for applications in Frascati tokamak upgrade.

S. Almagiva<sup>A</sup>, L. Caneve<sup>B</sup>, F. Colao<sup>\*B</sup>, R. Fantoni<sup>B</sup>, V. Lazic<sup>B</sup>, G. Maddaluno<sup>A</sup>, A. Palucci<sup>B</sup>.

<sup>A</sup>ENEA for EUROfusion C.R. Frascati, Via Enrico Fermi 45, 00044 Frascati, (Rome), Italy; <sup>B</sup>ENEA FSN-TECFIS C.R. Frascati, Via Enrico Fermi 45, 00044 Frascati, (Rome), Italy;

\*francesco.colao@enea.it

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**ABSTRACT:** Although not a concern in the present day tokamaks, to ensure safe operation of the next generation thermonuclear reactors like ITER (under construction in Cadarache, France) it is of fundamental importance to constantly monitor the content of tritium within the vacuum chamber. In fact, if one consider the need for an extended duty cycle of the next devices, ex-situ techniques will no longer be useful for monitoring of plasma facing components, so alternative methods are under study.

Among them, laser-based methods are under intense investigation [1] and LIBS is currently a promising candidate because of its prerogatives like sample preparation-free measurements, broad elemental coverage, including lighter elements, such as D, T, Be, in-situ- remote capabilities and thin-sample analysis (down to micrometric layers) without or reduced substrate interference.

In this contribution we present the development of a remote LIBS system to be applied to on the Frascati Tokamak Upgrade (FTU) fusion device, located at ENEA Frascati, capable to monitor the elemental composition, including retained deuterium, of the metallic components of the vacuum vessel. As next step, a new LIBS apparatus is planned to be realized on a robotic manipulator which will enter FTU vacuum vessel and monitor the erosion/deposition processes on large areas, during the maintenance shut-down period when the chamber is filled with inert gas (N<sub>2</sub>, Ar) at near atmospheric pressure. This application is intended to pave the way for a LIBS apparatus capable of tritium cartography in ITER.

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## **Analysis of Separation Processes for the Production of Radioisotopes Using Laser-Induced Breakdown Spectroscopy**

Kristian Myhre\*

Nuclear Security and Isotope Technology Division, Oak Ridge National Laboratory,  
Oak Ridge, Tennessee, United States

\*myhrekg@ornl.gov

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*ABSTRACT: Oak Ridge National Laboratory routinely produces a wide range of radioisotopes to meet the needs of both national and international communities. A prime example is the production of  $^{249}\text{Bk}$ , which is used as a target material for the discovery of super heavy elements, such as the recently named element Tennessine with atomic number 117. Oak Ridge National Laboratory's Radiochemical Engineering Development Center plays a key role in the production of these radioisotopes by performing radiochemical processing operations. A critical aspect of these operations is the routine quantitative elemental analysis of samples to determine the effectiveness of separations as well as impurities in the process. A Laser-Induced Breakdown Spectroscopy system is in use at the Radiochemical Engineering Development Center to explore techniques for quantitative elemental analysis of samples relevant to radioisotope separation processes. Results from recent work on performing these types of analyses will be presented and discussed. This will include the quantitative analysis of europium and samarium in an aluminum oxide matrix using both univariate and multivariate approaches.*

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## Quantitative Raman Microspectrometry of Uranium in Individual Aerosols over a Model Nuclear Atmosphere

Wabwire J.M. <sup>\*A</sup>, Angeyo K. H. <sup>B</sup>, Dehayem-Massop A. <sup>A</sup>,

Department of Physics, University of Nairobi, P.O. Box 30197-00100, Nairobi-Kenya \*  
jmwabwire@students.uonbi.ac.ke

**ABSTRACT:** Mining and processing of uranium including transformations in the nuclear fuel cycle often is accompanied by their immobilization and translocation to the environment. Capability for direct rapid analysis of micro-size particles such as aerosols in the environment is therefore a powerful tool to monitor undeclared nuclear activity. The strength of particle analysis is that it allows detecting very small amounts of nuclear material exhibiting an undeclared forensic signature. In this work, size - resolved ( $\Phi$ : 2.5 $\mu\text{m}$ , 4.5 $\mu\text{m}$ ) analysis of individual aerosols sampled from a radiogenically stressed ambient (to mimic a uranium mine environment) was undertaken in the context of in-field nuclear forensics. Sampling was achieved using a low volume cascade impactor with Al as the impaction substrate. Average loads of 0.002 g per substrate were maintained to avoid particle agglomeration. This made it possible to visualize individual particles using imaging mode confocal laser Raman spectrometry (microspectrometry) equipped with two CW lasers (beam size 0.1 $\mu\text{m}$ ) exciting at  $\lambda = 532 \text{ nm}$  and  $\lambda = 785 \text{ nm}$  to detect and quantify the uranium. Conventional analytical techniques that are suitable for such tasks e.g. SEM, SIMS are invasive and involve tedious sample preparation. Although trace and ultra-trace quantitative Raman spectroscopy is not yet fully developed, confocal laser Raman spectroscopy (CLRS) has the potential. It is also noninvasive and capable of in situ molecular identification to micron level resolution hence giving in-depth tenacity of chemical information of a sample. However, the data obtained is normally multivariate, complex and hyperspectral hence posing interpretative challenges. To overcome these limitations, we coupled CLRS with machine learning techniques namely PCA (for uranium spectral feature selection and data dimension reduction) and ANN (based on newfeed forward and cascade backpropagation algorithms) for developing a multivariate calibration strategy to realize the quantification of uranium. Standard uranyl nitrate and coating deposition on four substrates (Perspex, silicon wafers, glass and aluminum) were used to find out the one that best enhanced the Raman scatter signal. Perspex was the best. We report strong Raman scatter peaks at 825/ 841 $\text{cm}^{-1}$ , 863 $\text{cm}^{-1}$ , and 868 $\text{cm}^{-1}$  all of which were assigned to the symmetric vibrational stretching of the U-O bond. These may be considered as nuclear forensic signatures for identification of uranium-bearing nuclear materials and hot aerosols in the atmosphere. Using feature selection, the bands at 841  $\text{cm}^{-1}$ , 863  $\text{cm}^{-1}$  and 868  $\text{cm}^{-1}$  were utilized simultaneously for quantification purposes. The  $R^2$  value obtained was 0.96 with REP  $\leq 10\%$ . The limit of detection was found to be 43 ppb (for PM<sub>4.5</sub>.) Validation of the analytical method for quantitative analysis was done using a synthetic membrane standard based on the IAEA-RGU 1 certified reference material and the accuracy found to be  $\leq 10\%$ . Depending on the sampling location, the concentration of uranium in the aerosols ranged 50-200 ppb, being more enriched in the 4.5  $\mu\text{m}$  compared to the 2.5  $\mu\text{m}$  size fraction, which shows the source of the uranium was mostly the immediate surrounding as opposed to long range transport to the study area. PCA (based on loadings and score plots) classified the particles based on their sampling source fields. This is a powerful way to perform source attribution of nuclear materials exploiting the uranium Raman scatter peaks as nuclear forensic signatures. This work has also demonstrated the usefulness of machine learning enabled CLRS for rapid direct quantitative determination of radioactive contamination sources in the environment in the context of nuclear security and safeguards monitoring.

## Simultaneous echelle broadband and high resolution OES study for CF LIBS analysis of W-based materials in thermonuclear fusion.

Pavel Veis<sup>\*A</sup>, Michal Anguš<sup>A</sup>, Júlia Miškovičová<sup>A</sup>, Mária Suchoňová<sup>A</sup>

<sup>A</sup>Department of Experimental Physics, Comenius University, Faculty of Mathematics Physics and Informatics, Mlynska dolina F2, 842 48 Bratislava, Slovakia.

\*pavel.veis@fmph.uniba.sk

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**ABSTRACT:** Tungsten and tungsten based layers (BeW, AlW,...) has been widely studied as candidate material for divertor plasma facing components in thermonuclear fusion devices. Calibration free laser induced breakdown spectroscopy (CF LIBS) seems to be the most suitable technique for "in-situ" calibration to quantify the retained fuel (deuterium and in future tritium) amount in W-based materials [1,2] as well as for "in-situ" elemental analysis of wall material of fusion devices [3,4]. This technique requires accurate determination of the electron density and temperature of the LIBS plasma. The use of W III lines in Saha-Boltzmann plot helps to more precise electron temperature evaluation [5]. The W III lines are mainly presented in vacuum UV range. The fuel retention evaluation in future ITER wall is planned to be realised at atmospheric pressure conditions so it means that the use of vacuum UV spectral range will not be possible. Tungsten has huge number of spectral lines in UV-NIR spectral range the probability of overlapping is quite high. Moreover, the atmospheric pressure LIBS provide higher ablation rate as low pressure LIBS. Higher particles densities at atmospheric pressure leading to the possible self-absorption phenomena. Simultaneous echelle type broadband spectroscopy and high resolution optical emission spectroscopy (OES) enable us to scan whole UV and partially visible spectral range provide the correct choice of non-overlapped and non-self-absorbed W I-II lines, which is necessary for future fuel retention evaluation. Finally in order to test the choice of spectral lines we test the set of line on CF LIBS analysis of tungsten welding electrode (with small addition of other elements up to 2 %). The high-resolution (THR 1500, Jobin Yvon) and a broadband echelle type spectrometer (Mechelle ME5000, Andor Technology), both coupled with an iCCD camera (iStar DH734, Andor Technology) were used for the simultaneous measurements. The evaluation of the main plasma parameters (electron temperature and density) was studied as a function of different parameters (gate delay and width, laser fluence). [1] K. Piip, G. De Temmerman et al., J. Nucl. Mater. 47 (2015) 919 [2] A. Lisovski, K. Piip, L. Hämarik et al., J. Nucl. Mater. 47 (2014) 923 [3] R. Fantoni, S. Almaviva, L. Caneve, F. Colao, A.M. Popov, G. Maddaluno; Spectrochim. Acta, Part B 87 (2013) 153–160 [4] M. Suchoňová, J. Krištof, M. Pribula, M. Veis, F.L. Tabarés and P. Veis, Analysis of LiSn alloy at several depths using LIBS, Fusion Eng. Des [5] M.Pribula, M.Suchoňová, A.Hakola, P.Veis et al, Physica Scripta, T167, 2016, Art. Nb. 014045

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## Vacuum Ultraviolet Laser Induced Breakdown Spectroscopy (VUV-LIBS) For Pharmaceutical Analysis.

M. B. Alli and P. Hayden

School of Physical Sciences and NCPST, Dublin City University, Glasnevin, Dublin 9, Ireland

\* muhammed.alli2@mail.dcu.ie

**ABSTRACT:** As an analytical technique, Laser Induced Breakdown Spectroscopy (LIBS) allows quick analysis to determine the composition of the target. Samples need little/no preparation, removing the risk of contamination or loss of analyte [1]. It is minimally ablative so negligible amounts of sample is destroyed, while allowing quantitative and qualitative results [1]. VUV-LIBS [2, 3], due to the abundance of transitions at shorter wavelengths [4], offers improvements over LIBS in the visible region, such as achieving lower limits of detection for trace elements and extends LIBS to elements/samples not suitable to visible LIBS.

These qualities also make VUV-LIBS attractive for pharmaceutical analysis. Due to success in the pharmaceutical sector molecules representing the Active Pharmaceutical Ingredients (API) have become increasingly complex.

These organic compounds reveal spectra densely populated with carbon and oxygen lines in the visible and infrared regions, making it increasingly difficult to identify an inorganic analyte.

The vacuum ultraviolet region poses a solution as there is much better spacing between spectral lines.

VUV-LIBS experiments were carried out on Pharmaceutical Samples and Chemometric techniques were applied to analyse the samples [5-7]. The motivation for the application of these Chemometric techniques is the classification of analytes, allowing us to distinguish pharmaceuticals from one another based on their spectra.

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## Analysis of the roles of trace elements in malignant breast tumor in canine patients using Energy Dispersive X-ray Fluorescence (EDXRF) Technique

S.S. Sakamoto<sup>A</sup>, A.L. Andrade<sup>B</sup>, M.C.R. Luvizotto<sup>B</sup>, Ferreira G.T.N.M.<sup>B</sup>, M. Scapin<sup>C</sup>,  
A. Antunes<sup>\*D,E</sup>

<sup>A</sup> Faculdade Católica do Tocantins-Brazil; <sup>B</sup> Universidade Estadual Paulista – UNESP, Campus de Araçatuba, Curso de Medicina Veterinária-Brazil; <sup>C</sup> Instituto de Pesquisas Energéticas e Nucleares IPEN-CNEN/SP-Brazil; <sup>D</sup> Departamento de Física - Faculdade de Ciências e Tecnologia, Universidade, Nova de Lisboa, Campus da Caparica, Portugal; <sup>E</sup> Instituto de Física, Universidade Federal de Uberlândia, Uberlândia, Brazil.

\*andrea.antunes@ufu.br

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**ABSTRACT:** *The present study was intended to determine trace element in female dogs with malignant breast cancer. The mammary tumours were removed by simple mastectomy or regional mastectomy [5] with or without the superficial inguinal lymph nodes. The neoplasm tissue samples measured were collected during the routine surgical procedures performed. A total of 34 dogs with clinically evaluated diagnosis of malignant breast tumor. The canine patients were divided into three groups, complex carcinoma (n=25), tubulopapillary carcinoma (n=9) and healthy mammary glands as control group (n=10). Analyses were performed using Energy Dispersive X-Ray Fluorescence equipment. Our results suggest an increase in Fe concentration in malignant tumors, particularly in the complex carcinoma. To tubulopapillary carcinoma group the trace element predominant was Cu concentration confirming the hypothesis proposed in literature to humans which has indicated that Cu is cumulated in the neoplastic tumours of the mammary gland.*

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## Monitoring the incorporation of hydroxyapatite on chitosan scaffolds using LIBS.

A. Antunes<sup>\*A,B</sup>, J. S. Cabral<sup>B</sup>, B. Sakamoto<sup>B</sup>, G. Nicolodelli<sup>C</sup>, D. M. B. P.C. Milori<sup>C</sup>, M. F. Raposo<sup>A</sup>

<sup>A</sup> Departamento de Física - Faculdade de Ciências e Tecnologia, Universidade, Nova de Lisboa, Campus da Caparica, Portugal; <sup>B</sup> Instituto de Física, Universidade Federal de Uberlândia, Uberlândia, Brasil; <sup>C</sup> Embrapa Instrumentação, São Carlos, Brasil.

\*andrea.antunes@ufu.br

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**ABSTRACT:** Tissue engineering corresponds to promising approach for the development of biological substitutes that regenerate, maintain or restore the function of damaged tissue. Our objectives were to produce chitosan/hydroxyapatite scaffolds with different densities and to characterize three-dimensional structures based for use in biomedical applications. Laser-Induced Breakdown Spectroscopy (LIBS) is an experimental technique used to determination of trace elements constituents or present in the matter. In this work, we have used LIBS to verify position of incorporation of hydroxyapatite (HA) in the scaffold. The experimental setup used a Q-switched Nd:YAG laser to be the laser source and equipped with an eight-channel model spectrometer which is wavelength range between 200 and 1100 nm. LIBS results obtained showed majority elements as Ca, P in different points of the samples, minor elements were analyzed. Scanning electron microscopy (SEM) and Atomic force Microscopy results indicated that the bone composite scaffolds produced have a well-defined structure with pore size of 100 to 300  $\mu\text{m}$ .

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## Local Production or Imported Gods? Multi-analytical Investigations of Archaeological Glazed Ceramics (XVI<sup>th</sup>-XVIII<sup>th</sup> centuries) from Largo do Jesus, Lisbon

Pedro Barrulas<sup>A</sup>, Massimo Beltrame<sup>A,B</sup>, Guilherme Cardoso<sup>A</sup>, Anne-France Maurer<sup>A</sup>, José Mirão<sup>A</sup>, António Candeias<sup>\*A</sup>

<sup>A</sup> HERCULES Laboratory, University of Évora, Largo Marquês de Marialva, 8, 7000, Évora, Portugal;  
<sup>B</sup> CIDEHUS, Interdisciplinary Centre for History, Culture and Society - Largo Marquês de Marialva, 8, 7000, Évora, Portugal; <sup>C</sup> Archaeological Centre of Lisbon, Avenida da Índia 166, 1400-038, Lisbon, Portugal

\*candeias@uevora.pt

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**ABSTRACT:** The archaeological investigation carried out at the Largo de Jesus archaeological site (Mercês, Lisbon) in 2005, allowed the identification of several archaeological realities that trace the history of this area since the XVI<sup>th</sup> century. Amongst these realities it is important to mention the discovery of a big housing area and the remains of a probable ceramic production area. During the excavation different archaeological artefacts were found such as common ceramics, glazed ceramics, faiences (blue over blue, blue over white, white and black over white decorations), porcelains, glasses and bone decorative objects. In particular, faience showed a considerable typological diversification. Questions about “How were these materials produced?” and “From where came the raw materials employed?” drove us to start a multi-analytical approach to answer these questions, focused mainly on this typology of glazed ceramic objects. 23 samples were selected and micro sampled for the analysis of the clay matrix and also of the glazed decoration. Bulk analysis was performed using portable XRF spectrometer, mineralogical analysis were done by  $\mu$ -XRD, while micro-structural analysis was performed on the glaze and on the ceramic body of the samples by SEM-EDS. Information about the trace element content on the glaze of the samples was obtained through micro-analysis using LA-ICP-MS. The knowledge about the trace elemental composition showed to be of extreme importance for elemental fingerprinting of the glaze decoration, leading us to distinguish and attribute the origin of the different studied artefacts. Preliminary analysis of lead isotopic composition was also tested in order to provide additional information about provenance and technology.

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## Bioconjugated supramolecular exo-functionalized palladium cages to peptides for biomedical applications

Jiaying Han<sup>\*A</sup>, Andrea Schmidt<sup>B</sup>, Hjalmar P. Permentier<sup>A</sup>, Rainer Bischoff<sup>A</sup>,  
Peter Horvatovich<sup>A</sup>, Angela Casini<sup>A,C</sup>

<sup>A</sup>Department of Analytical Biochemistry, Groningen Research Institute of Pharmacy, University of Groningen, Antonius Deusinglaan 1, 9713 AV Groningen; <sup>B</sup>Catalysis Research Center, Technische Universität München, Ernst-Otto-Fischer-Str. 1, 85747 Garching bei München, Germany; <sup>C</sup>School of Chemistry, Cardiff University, Park Place, CF103AT Cardiff, UK

\*jiaying.han@rug.nl

**ABSTRACT:** Supramolecular coordination complexes (SCCs) offer new opportunities for improved drug delivery systems by well-defined internal cavities and relatively facile pre- or post-self-assembly functionalization. These properties augment the modularity of the directional bonding design strategy to provide structures with unprecedented fine-tuning possibilities, spatially and electronically.

A specific and attractive area of SCCs is the self-assembly of  $M_2L_4$  ( $M$  = metal,  $L$  = ligand) metallacages, which can enclose a wide range of small molecules within their cavity, both ions and neutral molecules. Recently, our group investigated fluorescent palladium(II)  $Pd_2L_4$  cages (with  $L$  being exo-functionalized bipyridyl ligands) as drug delivery systems for cisplatin, which proved to be active in cancer cells, while showing low ex vivo toxicity in healthy rat liver tissue. The obtained metallacages showed fluorescence properties due to the used ligand system. Similarly, exo-functionalized cages with naphthalene or anthracene groups, or featuring Ru(II) pyridine complexes, were studied with the aim to image their fate in cells via fluorescence microscopy. With the aim of implementing supramolecular metallacages as drug delivery systems, we report the first example of bioconjugation of self-assembled  $Pd_2L_4$  cages to the model linear peptide Ac-NLEFK-Am.

The obtained results open the possibility of efficient bioconjugation of metallacages to peptides which could be extended to targeting moieties such as cyclic RGD peptides or affimers, and possibly also to antibodies. This opportunity is particularly attractive in the case of metallacages encapsulating anticancer drugs (e.g. cisplatin) in order to efficiently target them to cancer cells. Two approaches of bioconjugation of metallacages to peptides have been attempted, both based on amide bond formation between the carboxylic acid (or amine) serving as exo-functionalized ligand/cage and the amine (or carboxylic acid) groups of the model peptide side-chains. So far the best results were achieved with the approach where first the coupling of the peptide to the ligands constituting the cages was performed, followed by in situ reconstitution of the  $Pd_2L_4$  cages via self-assembly. Future research in our group will focus on tethering  $Pd_2L_4$  cages to targeting peptides such as cyclic RGD peptide and to investigate the activity of the supramolecular-cisplatin bioconjugate in cancer cells and tissues.

## Catalytic N-dealkylation of Drug Molecules on a Nanoporous Gold Surface

Tao Yuan<sup>A</sup>, Jiquan Wu<sup>B</sup>, Tao Zhang<sup>A</sup>, Petra Rudolf<sup>AB</sup>, Rainer Bischoff<sup>A</sup>, Hjalmar Permentier<sup>\*A</sup>

<sup>A</sup>Analytical Biochemistry, University of Groningen, A Deusinglaan 1, Groningen, The Netherlands; <sup>B</sup>Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, Groningen, The Netherlands

\*h.p.permentier@rug.nl

**ABSTRACT:** Nanoporous gold (NPG) has attracted considerable interest for application in heterogeneous catalysis, electrocatalysis, fuel cells and biosensing. NPG is fabricated by dealloying a gold alloy containing a less noble constituent, such as silver or copper, resulting in a three-dimensional sponge-like porous network structure with a nanopore size of 10-100 nm. NPG has the merits of a large interface-to-volume ratio, good conductivity, ease of preparation and tunable pore size. It has been used as a catalyst for oxidation of simple molecules, for example the conversion of CO to CO<sub>2</sub> and oxidation of methanol to formic acid. We have, for the first time, employed NPG for reactions of more complex drug molecules, with the aim of synthesizing drug metabolites of interest for pharmaceutical studies.

A nanoporous gold catalyst was prepared by incubation of a 5×5×0.5 mm piece of gold alloy in concentrated nitric acid for 24 h. The silver and copper in the alloy were mostly etched away, leaving behind a porous gold surface. Scanning electron microscope (SEM) characterization showed a homogeneous surface, with a nanopore size of 33.2±7.4 nm. With X-ray photoelectron spectroscopy (XPS) the amount of silver was determined to be decreased from 30% to 6.8%, and no other elements were detected. Electrochemical measurements indicated that the active area of the porous gold was 174 times larger than a pure gold electrode with the same geometric area.

The nanoporous gold surface was subsequently used as a catalyst for oxidative drug conversion. A high yield of N-dealkylation was observed for the drugs lidocaine and metoprolol (93% and 99% respectively), and the reaction was highly specific; no other oxidation products were detected. The turnover frequencies of lidocaine and metoprolol were 3.1 h<sup>-1</sup> and 4.3 h<sup>-1</sup> at 3 mM substrate concentration, air purging and a temperature of 60 °C. We are currently studying the reaction mechanism in more detail to determine the effect of the nanopore size, the residual silver amount and the role of oxygen. We are also studying more drug substrates to investigate the scope and selectivity of reactions that can be catalyzed by NPG.

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## Chemical characterization of a collection of metallic oil lamps from Gharb al-Andalus (Southern Portugal): An in-situ and non destructive approach by handheld X-Ray Fluorescence spectrometer and open source Monte Carlo simulation code.

Carlo Bottaini<sup>\*A,B</sup>, Antonio Brunetti<sup>C</sup>, José Mirão<sup>A,D</sup>, Helena Catarino<sup>E</sup>, António Candeias<sup>A,D</sup>, Rui J. Silva<sup>F</sup>

<sup>A</sup>HERCULES Laboratory, Escola de Ciências e Tecnologia, University of Évora, Palácio do Vimioso, Largo Marquês de Marialva 8, 7000-809 Évora, Portugal; <sup>B</sup>CIDEHUS, University of Évora, Palácio do Vimioso, Largo Marquês de Marialva 8, 7000-809 Évora, Portugal; <sup>C</sup>Dipartimento di Scienze Politiche, Scienze della Comunicazione e Ingegneria dell'Informazione, Università di Sassari, Piazza Università 21 – 07100 Sassari, Italy; <sup>D</sup>Escola de Ciências e Tecnologia, Colégio Luis António Verney, Rua Romão Ramalho, 59 - 7000-671 Évora; <sup>E</sup>FLUC/CEAACP, Instituto de Arqueologia. Palácio de Sub-Ripas, 3000 Coimbra, Portugal; <sup>F</sup>CENIMAT/I3N, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, Quinta da Torre, 2829-516 Caparica, Portugal.

\*carlo@uevora.pt

**ABSTRACT:** This paper presents the results of the chemical analysis carried out on a group of five oil lamps from the Islamic period (VIII-XIII century AD) found at different sites from Gharb al-Andalus (Southern Portugal). The analyzed artifacts are unique being the only metallic oil lamps known at the moment in the region. From a morphological point of view, they show affinities with objects found at Islamic sites both in the Iberian Peninsula and the Central Mediterranean, namely Sicily [1]. Thus, the oil lamps from Gharb al-Andalus could represent rare local productions or imported artifacts. Due to the exceptional nature of the analyzed oil lamps and also taking into account the brittleness of the artifacts, the chemical analysis was carried out according to a completely non-destructive approach. This was possible thanks to the recent development of a novelty spectroscopic protocol combining Energy Dispersive X-Ray Fluorescence Spectrometry (ED-XRF) with an open source Monte Carlo (MC) simulation algorithm named XPMC. Theoretical-experimental studies [2-3] and recent case study applications [4] have shown that this protocol is able to determine the chemical composition of the bulk metal with no need to remove samples or clean small areas of the analyzed artifacts. In this paper, the data obtained through the ED-XRF/MC protocol served a twofold purpose: a) to characterize the alloys used to produce the oil lamps, and b) to assess whether their production could be identified as local or non-local. The study is part of the project “DE RE METALLICA - Defining and Rediscovering Metallurgy and Trade in AL-Andalus (VIII-XIII century AD): Leaping into Innovative Comprehensive Archaeometric Approaches”, funded by the Portuguese Science Foundation (FCT-MCTES) through the grant SFRH/BPD/111039/2015 (CB). The work was also funded by FEDER funds through the COMPETE 2020 Programme, Portugal2020 and by National Funds through FCT under the projects UID/Multi/04449/2013 (POCI-01-0145-FEDER-007649) (HERCULES Lab/UÉ), UID/HIS/00057/2013 (POCI-01-0145-FEDER-007702) (CIDEHUS/UÉ) and UID/CTM/50025/2013 (i3N/CENIMAT).

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## Nuragic votive swords from Sardinia (Italy): assessing alloy's composition by EDXRF/Monte Carlo Simulations.

Antonio Brunetti<sup>A</sup>, Anna Depalmas<sup>B</sup>, Nick Schiavon<sup>C</sup>

<sup>A</sup> POLCOMING Department, University of Sassari; <sup>B</sup> Dipartimento di Storia, Scienze dell'uomo e della Formazione, Università di Sassari, Italia; <sup>C</sup> Hercules Laboratory, University of Évora, Largo Marquês de Marialva 8, Évora, Portugal

\*sakka.tetsuo.2a@kyoto-u.ac.jp

**ABSTRACT:** Within the different typologies of metal weapons produced by the Nuragic civilization (Sardinia, Italy), from an archaeological perspective, the so-called votive swords show peculiar characteristics. The size of the blade is narrower and longer than usual [1-5] and their alloy composition makes them unsuitable for fighting. They appear to be religious objects. By determining their chemical composition information can be gained on the provenience and the production technology. However, the presence of thick and rough superficial patinas on alloy surfaces makes this analytical task difficult. In this study, EDXRF measurements combined with Monte Carlo simulations have been used. Some preliminary results are shown and discussed.

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## **Chemical methodologies for proteins analysis. A focus on conformational studies based on Fourier Transform Infrared Spectroscopy.**

Emilia Bramanti, Beatrice Campanella

National Research Council of Italy, C.N.R., Istituto di Chimica dei Composti Organo Metallici-ICCOM- UOS  
Pisa, Area di Ricerca, Via G. Moruzzi 1, 56124 Pisa (Italy)

\*[bramanti@pi.iccom.cnr.it](mailto:bramanti@pi.iccom.cnr.it)

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*ABSTRACT: This lecture will focus on proteins and on one of the most common spectroscopic method employed to study their conformation, Fourier Transform Infrared Spectroscopy (FTIR). Proteins are amino acid polymers responsible for implementing instructions contained within the genetic code. Each protein formed in the body participates in processes that characterize the individuality of cells, tissues, organs, and organ systems. A typical cell contains thousands of different proteins, each unique in its own structure and function. Protein function depends of their structure. FTIR spectroscopy allows us to investigate protein structure in term of percentage of protein secondary structure ( $\alpha$ -helices,  $\beta$ -structures, random coil), as well as to evidence structural changes caused by unfolding processes, protein-protein interactions and interaction with small molecules, aggregation processes due to their "misfolding". An example on the application of FTIR to the study of aggregation of 1-42 beta amyloid peptide, the protein involved in the Alzheimer disease, and other proteins will be discussed.*

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## Two paintings, similar gold leaf manufacturing? Nondestructive determination of gold leaf thickness in panel paintings

Vanessa Antunes<sup>A,B\*</sup>, Vitor Serrão<sup>A</sup>, António Candeias<sup>C,D</sup>, José Mirão<sup>D</sup>, Maria L. Carvalho<sup>B</sup>,  
Sofia Pessanha<sup>B</sup>, Natasha Fernandes<sup>F</sup>, Marta Manso<sup>B,G</sup>

<sup>A</sup>ARTIS-Instituto História da Arte, Faculdade de Letras, Universidade de Lisboa (ARTIS-FLUL), Alameda da Universidade, 1600-214 Lisboa, Portugal; <sup>B</sup>LIBPhys-UNL, Laboratório de Instrumentação, Engenharia Biomédica e Física da Radiação, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516, Caparica, Portugal; <sup>C</sup>Laboratório José de Figueiredo, Direcção-Geral do Património Cultural (LJF-DGPC), Rua das Janelas Verdes 37, 1249-018 Lisboa, Portugal; <sup>D</sup>Laboratório HERCULES, Escola de Ciências e Tecnologia, Universidade de Évora, Largo Marquês de Marialva 8, 7000-676 Évora, Portugal; <sup>E</sup>CHAIA- Centro de História da Arte e Investigação Artística, Palácio do Vimioso, Largo Marquês de Marialva, nº8, 7002-554 Évora; <sup>F</sup>Museum of Christian Art, Convent of Santa Monica, Old Goa, Goa; <sup>G</sup>Faculdade de Belas-Artes, Universidade de Lisboa, Largo da Academia Nacional de Belas-Artes, 1249-058 Lisboa, Portugal.

\*vanessahantunes@gmail.com

**ABSTRACT:** This work compares the gold leaf employed in two paintings in order to understand their original manufacture. The two paintings, from the 18<sup>th</sup> century, concern the same series but different themes: *Our Lady of Sorrows* and *Our Lady of Seven Sorrows*. Framed with flowers and hanging coloured striped ribbons in a black background, with the Virgin in the center, these paintings are inspired by baroque Portuguese models [1, 2]. The panel paintings are polychrome and gilt, being nowadays in Museum of Christian Art, Convent of Santa Monica, Old Goa, Goa. A third painting was found in the collection of Xavier Centre of Historical Research, Porvorim, Goa, being probably from the same series. When comparing the thickness measures of the three paintings we can find similar values between the paintings, showing a probable relation to the same series. The aim of this study is to compare the gold leaf thickness in different paintings from the same period and series. Using energy dispersive X-ray fluorescence and comparing the attenuation of the different characteristic lines of gold measured in different parts of the gold leaves [3, 4]. To perform this study, the materials were analyzed also by Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy in one sample taken from each gold leaf painting in order to confirm the thickness results obtained by energy dispersive X-ray fluorescence technique. This research brought a new insight to the study of thickness in gold leaves when applied in paintings with a noninvasive technique. The use of this methodology will contribute to the knowledge of the painting technique and preservation of paintings when concerning the determination of gold leaf thickness manufacturing.

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## Automatic classification of metal alloys from their LIBS spectra and its robustness against spectrometer decalibration

Adolfo Cobo<sup>\*A</sup>, Artzai Picón<sup>B</sup>, Marina Martínez<sup>A</sup>, Cristina López-Sarachaga<sup>B</sup>, Zuriñe Amondarain<sup>B</sup>, José Miguel López-Higuera<sup>A</sup>

<sup>A</sup>Photonics Engineering Group, University of Cantabria, 39005 Santander, Spain; <sup>B</sup>Tecnalia, Parque Tecnológico de Bizkaia, 48160 Derio- Bizkaia, Spain

\*adolfo.cobo@unican.es

**ABSTRACT:** Among the most successful applications of LIBS in the industry is the analysis of metal alloys and steel, mainly due to the rich information in the emitted spectra from minor and major constituents of the alloys, and the possibility of online, remote, and automated analysis. This opens the possibility of applications such as online quality monitoring of steel production [1] or automated metal scrap sorting [2]. For these tasks, the raw spectra should be processed and transformed into meaningful information, such as composition, quality deviations or detection of valuable, toxic or specific elements, and several chemometric or artificial-intelligent based techniques have been proposed [3]. All these approaches should cope with the possibility of long-term wavelength decalibration of the spectrometer, especially for low-cost CCD spectrometers and in the tough manufacturing environment.

In this work, we report on the automatic classification of steel alloys samples based on their LIBS spectra generated with a Nd:YAG laser @ 1064nm and captured in the 240-518nm spectral range. The samples have been manufactured in a levitation melting induction furnace and contains different known percentage of single elements in iron: C, P, Mo, S, Mn, Cr, Cu, Sn, Si, Ni, and Al. The thousands of LIBS spectra collected from each sample have been used to train a deep autoencoder neural network [4] to perform the classification, and performance numbers have been obtained. As only the raw spectra with no peak identification or modelling have been passed onto the classifier, the classification rate decreases significantly if data from experiments in different days with small wavelength decalibration is used to validate the trained network. To ensure the long-term operation in a real application, several approaches have been tested, among others: periodic auto-recalibration based on the iron emission lines, data augmentation with purposely decalibrated spectra for the network training or Bayesian estimation of the deviations on the calibration function on a fully Bayesian approach. Results show the robustness of these approaches.

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## Degradation assessment of parchment manuscript at macro- and molecular level using an non-invasive approach

Ioana Maria Cortea<sup>\*A</sup>, Luminița Ghervase<sup>A</sup>, Roxana Rădvan<sup>A</sup>, Lucian Ratoiu<sup>A</sup>

<sup>A</sup>Department of Optoelectronic Methods and Techniques for Artwork Restoration and Conservation, National Institute for Research and Development in Optoelectronics, 409 Atomistilor St., Magurele, Romania.

\*ioana.cortea@inoe.ro

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**ABSTRACT:** *This paper describes the use of a multi-analytical non-invasive approach carried on a Jewish ritual parchment. The manuscript, undated, belonging to a private collection, was found in a precarious state of conservation probably due to improper storage conditions. In order to evaluate the state of degradation, the surface and interior of the parchment scroll were examined using Multi- and Hyperspectral Imaging, Fourier Transform Infrared (FTIR) Spectroscopy and X-ray Fluorescence (XRF). Spectral imaging allowed identification and mapping of the various stages of intervention that the manuscript went through, marks of previous conservation interventions, as well as highlights regarding specific forms of degradation and their distribution within the surface of the manuscript. Results of the FTIR analyses offered an in depth view regarding the deterioration rate of the collagen material, denaturation of proteins being observed mainly via the Amide II band shift towards lower wavenumbers. In addition, information regarding the preparation of the parchment itself was obtained, the presence of calcium carbonate being assessed in all analyzed areas. Regarding ink chemical composition, XRF analysis shows Fe, Mn, S, K and Cr as major elements, while spectral features from the hyperspectral data, combined with laboratory samples, points towards a carbon black ink mixed with iron gall. The results of the combined analyses shows a highly heterogeneous matrix, with various level of oxidation of the polypeptide chain, with darker and ink areas showing a higher degree of degradation, possible as a result of ink oxidation and/or interaction of the ink components with the collagen fibres. Interesting details are given by registered X-ray emission lines of Ag and Cu, higher within the darker areas, as well as traces of Zn, the presence of these elements raising questions about the history of the object, manufacture technique and past conservation treatments.*

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## Multi-analytical approach to the study of the European glass beads found in the tombs of the Church of Kulumbimbi (Angola)

Mafalda Costa<sup>A,B</sup>, Pedro Barrulas<sup>B</sup>, Maria da Conceição Lopes<sup>C,D</sup>, João Barreira<sup>C</sup>, Bernard Clist<sup>E</sup>, Karlis Karklins<sup>F</sup>, Koen Bostoen<sup>E</sup>, Maria da Piedade de Jesus<sup>G</sup>, Sónia da Silva Domingos<sup>G</sup>, Luc Moens<sup>H</sup>, Peter Vandenabeele<sup>A</sup>, José Mirão<sup>B,I\*</sup>

<sup>A</sup>Department of Archaeology, Archaeometry Research Group, Ghent University, Sint-Pietersnieuwstraat 35, B-9000 Ghent, Belgium; <sup>B</sup>HERCULES Laboratory, University of Évora, Palácio do Vimioso, Largo Marquês de Marialva 8, 7000-554 Évora, Portugal; <sup>C</sup>Research Center in Archaeology, Arts and Heritage Sciences, University of Coimbra, Palácio de Sub-Ripas, 3000-395 Coimbra, Portugal; <sup>D</sup>Department of History, Archaeology and Arts, Faculty of Arts and Humanities, University of Coimbra, Largo da Porta Férrea, 3004-530 Coimbra, Portugal; <sup>E</sup>Department of Languages and Cultures, BantUGent – UGent Centre for Bantu Studies, Ghent University, Blandijnberg 2, 9000 Ghent, Belgium; <sup>F</sup>Society of Bead Researchers, Ottawa, Canada; <sup>G</sup>Instituto Nacional do Património Cultural (INPC), Rua Major Kanhangulo, 77/79, CP1267, Luanda, Angola; <sup>H</sup>Department of Analytical Chemistry, Raman Spectroscopy Research Group, Ghent University, S-12, Krijgslaan 281, B-9000 Ghent, Belgium; <sup>I</sup>Department of Geosciences, School of Science and Technology, University of Évora, Colégio Luís António Verney, R. Romão Ramalho, 59, 7000-671 Évora, Portugal.

\*jmirao@uevora.pt

**ABSTRACT:** The Portuguese navigator Diogo Cão first came into contact with the Kongo kingdom when he reached the mouth of the Congo River in 1483<sup>1</sup>. Contact with the Portuguese had a huge impact in the Kongolese society, and many Portuguese practices were readily adopted, especially religion and literacy<sup>1,2</sup>. The oceanic trade routes introduced by the Portuguese in the end of the 15<sup>th</sup> century also allowed a massive influx of European manufactured goods, such as glass beads, ceramics and fire arms<sup>3</sup>. The glass beads, used as adornments or amulets, were a symbol of wealth, social status and political, cultural and religious affiliation<sup>3,4</sup>. This makes the study of European trade beads particularly important since it can shed light on economic interactions and consumption patterns on a chronological level<sup>3</sup>.

A collection of over 3000 glass beads were recovered during the 2015 excavation campaign in the ruins of the Church of Kulumbimbi (formerly known as Cathedral of São Salvador), Mbanza Kongo, Angola. The current name Kulumbimbi, which originated in the Oral Traditions, means "what remained of the ancestors" in Kikongo<sup>5</sup>.

In order to determine the composition of these glass beads, a multi-analytical minimally invasive methodology was applied, which includes handheld X-ray fluorescence (hXRF), micro X-ray diffraction ( $\mu$ -XRD), variable pressure scanning electron microscope coupled with energy dispersive X-ray spectrometry (VP-SEM-EDS), micro-Raman spectroscopy and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

The results were interpreted considering probable provenance, raw materials used and technology available in the production of these artefacts. Especial effort was made to understand the processes of glass colouring and opacification.

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## Bayesian Naïve Classification for LIBS

Damien Devismes<sup>\*A</sup>, Frédéric Pelascini<sup>A</sup>

<sup>A</sup>CRITT Matériaux Alsace, Schiltigheim, France.

\*d.devismes@critt.fr

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**ABSTRACT:** Widely used in the Big Data<sup>1</sup>, medical diagnosis<sup>2</sup>, archeology<sup>3</sup> or text classifications, the Bayesian Inference (BI) are taking a higher importance recently. However, it is still unknown in many communities including the LIBS community. The Bayesian Naïve Classification (BNC) is based on the BI and works as a linear classifier which provides a strong independence of the hypothesis. In this case, the aim of this classification is based on the maximum likelihood estimation. The Bayes theorem (1) derives the posterior probability as a consequence of two antecedents, a prior probability and a 'likelihood fonction'. And then so the BNC adds a classifier of the maximum a priori.

$$P(H|E) = [ P(E|H).P(H) ] / P(E) \quad (1)$$

The interest of the BNC is that despite a simple algorithm, it is known to obtain surprising results. The goal of this work is to determine if the BNC can be applied to the LIBS spectra and to describe the possibilities and the limits.

To adapt this method to the LIBS spectra we used the approach explained shortly here after. For each reference material, we treated several spectra in order to extract for each peaks of interest, its average value and its standard deviation. In a similar way, we extracted the intensity of the same peaks in the spectrum of the unknown material. Then for each peak we determined the probability that the value of the peak of the unknown material relates to the normal probability distribution of this peak of a reference material. And we repeat the process for each peak and then for each material of reference. The product of these probabilities is the posterior probability. Later, we classify the results of the references materials based on the maximum a priori.

Among the multiple strengths of the BNC, we count the simplicity of the algorithm and the multiple opportunities (e.g. highest posterior density for quantification with few data) we could implement in the future. We also know that it can't reach the success rate of classification of neuronal networks, nevertheless to treat quickly big data files of millions of spectra and tens of peaks of interests, the BNC should be a promising approach.

Here we will present the results given by one of the several implementations we are working on and we will discuss about the multiple interests of the BI.

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## The source of the building stones from the Sagunto Castle archaeological area and its surroundings

Gianni Gallelo\*<sup>AB</sup>, Mirco Ramacciotti<sup>B</sup>, Marco Lezzerini<sup>CD</sup>, Emilia Hernandez<sup>E</sup>, Matias Calvo<sup>E</sup>, Angel Morales<sup>B</sup>, Agustin Pastor<sup>B</sup>, Miguel De la Guardia<sup>B</sup>

<sup>A</sup>Department of Archaeology University of York, King's Manor York YO17EP, UK; <sup>B</sup>Department of Analytical Chemistry University of Valencia, 50 Dr. Moliner Street, 46100 Burjassot, Valencia Spain; <sup>C</sup>Department of Earth Sciences, University of Pisa, Via S. Maria 53, 56126 Pisa, Italy; <sup>D</sup>Applied and Laser Spectroscopy Lab., ICCOM-CNR, Via G. Moruzzi 1, 56124 Pisa, Italy; <sup>E</sup>Sagunto Archaeological Museum 23 del Castillo Street, 46500 Sagunto, Valencia, Spain.

\*Gianni.gallelo@york.ac.uk

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**ABSTRACT:** A multidisciplinary study was carried out on the building stones of the masonries belonging to the Castle of Sagunto (Valencia, Spain), an important historical and archeological complex, characterized by several construction phases from the Roman Period to the Modern Ages. For the first time, the stones of the Sagunto Castle have been analysed to determine their chemical, mineralogical and petrographic features, the main physical and mechanical properties, and to understand their decay, use and recycling dynamics in the different building during the entire occupational period. Geochemical and mineralogical analyses employing X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS) and X-ray diffraction (XRD) were carried out together with optical and electronic microscope analysis to observe the stone macro- and micro-structures. The collected data were processed by Principal Component Analysis (PCA) to highlight differences among the studied structures. The results show that the stones employed to build Sagunto's structures during the different historical periods are related to a specific quarried area located nearby Sagunto Castle hill and differences between the studied samples are mostly related to the conservation state of the buildings. Therefore, geochemical analyses confirm the origin of the raw materials, while petrographic and physical analyses have been useful to evaluate the conservation state of the studied Sagunto Castle structures.

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## Use of CaCl for the direct determination of Cl by high-resolution Continuum source graphite furnace molecular absorption spectrometry

Esperanza García-Ruiz,<sup>a</sup> Ananda Guarda,<sup>b</sup> Irene Andrés,<sup>a</sup> Maite Aramendia,<sup>c</sup> Paulo Cícero do Nascimento,<sup>b</sup> Martín Resano<sup>a</sup>

<sup>a</sup>Department of Analytical Chemistry, Aragón Institute of Engineering Research, University of Zaragoza, 50009, Spain; <sup>b</sup>Department of Chemistry, Federal University of Santa Maria, C.P. 5051, 97105-970 Santa Maria - RS, Brazil; <sup>c</sup>Centro Universitario de la Defensa de Zaragoza, Academia General Militar de Zaragoza, Carretera de Huesca s/n, 50090 Zaragoza, Spain

\*garciae@unizar.es

**ABSTRACT:** This work investigates the possibilities of high-resolution continuum source graphite furnace molecular absorption spectrometry for the direct determination of Cl in solid samples via the CaCl molecule and measurement of its molecular absorption. The method proposed is based on addition of 400 µg Ca as molecule-forming reagent and of 20 µg Pd as chemical modifier, which helps to stabilize the analyte and enhances sensitivity.

The molecular spectrum for CaCl offers different lines with different limits of detection and linear ranges, which permitted to analyze solid samples with different Cl contents. The lowest limit of detection (0.75 ng Cl, corresponding to 0.75 µg g<sup>-1</sup> for a typical sample mass of 1 mg) could be achieved by combination of three of the most sensitive lines in the vicinity of 620.862 nm, while the amplest linear range (up to 860 ng Cl) was achieved by selection of the less sensitive line at 377.501 nm.

The method developed enabled the direct determination of Cl in solid samples using simple external calibration with aqueous standards. Good precision (5–9% RSD) and accuracy was attained in a series of certified samples of very different nature (i.e. coal, iron oxide, polyethylene, human hair, pine needles, rice flour and milk) and with very different Cl contents, ranging from about 50 µg g<sup>-1</sup> to 1% (w/w) Cl. The method appears as particularly useful for Cl determination in samples with elevated Ca contents, for which biased results with other diatomic molecules, such as AlCl or SrCl, may be obtained.

### Acknowledgements

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## Nano-imaging of environmental dust in human lung tissue by Soft X-ray and hard XRF Microscopy

Alessandra Gianoncelli<sup>\*A</sup>, Clara Rizzardi<sup>B</sup>, Damien Salomon<sup>C</sup>, Vincenzo Canzonieri<sup>D</sup>, Lorella Pascolo<sup>B</sup>

<sup>A</sup> Elettra-Sincrotrone Trieste S.C.p.A., Strada Statale SS14, km 163.5, Basovizza 34149, Italy; <sup>B</sup> Department of Medical, Surgical, and Health Sciences, University of Trieste, Italy, Piazzale Europa 1, Trieste 34127, Italy; <sup>C</sup> Department of Medical, Surgical, and Health Sciences, University of Trieste, Italy, Piazzale Europa 1, Trieste 34127, Italy; <sup>D</sup> Division of Pathology, CRO Centro di Riferimento Oncologico, National Cancer Institute, IRCCS, Aviano (PN), Italy.

\*alessandra.gianoncelli@elettra.eu

**ABSTRACT:** It is well recognized that a large number of pulmonary diseases are induced by the effects of particulates in the inhalants [1]. As effect of environmental or occupational exposure, lung can present anthracosis, which is the condition occurring when carbon and other dust particles are found as a black pigment in the lung tissue and in the related lymph nodes. Carbon or coal dust pigment is virtually a ubiquitous air pollutant of urban life, so that such an asymptomatic accumulation can be found in varying degrees among most urban dwellers and in tobacco smokers. Since human health is progressively exposed to an increasing number and doses of anthropogenic nano/ultrafine compounds (particles), there is a pressing urgency to explore toxicological impact arising from these exposures and the molecular mechanisms driving the body defense or possible related diseases. The toxicity mechanisms are clearly related to chemical composition and physical and surface properties of materials. A combination of nano X-ray fluorescence imaging and soft X-ray microscopy was used to chemically characterize environmental particulates (anthracosis) in lung tissues from urban subjects. High-resolution XRF analyses performed at ESRF [3] and Elettra [4] synchrotrons allowed to discriminate single particles in the heterogeneous aggregates found in the lung tissue. The small particles have variable composition resulting from the different combinations of Ti with O, K and Si, Al and Si, or Zn and Fe with O. Interestingly, simultaneous absorption and phase contrast images showed the particulate morphology and allowed to predict the presence of very dense nanoparticles or high concentration of heavy elements.

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## Raman spectroscopy for the characterization of a polychromed marble decorative revetment from the Alhambra

González Cabrera, M.<sup>\*A</sup>, Arjonilla, P.<sup>A</sup>, de la Torre López, María José<sup>B</sup>, Correa Gómez, Elena<sup>C</sup>, Rubio Domene, Ramón<sup>C</sup>, Domínguez-Vidal, A.<sup>A</sup>, Ayora-Cañada, M.J.<sup>A</sup>

<sup>A</sup>Department of Physical and Analytical Chemistry, Universidad de Jaén, Campus Las Lagunillas, s/n, 23071, Jaén, Spain; <sup>B</sup>Department of Geology, Universidad de Jaén, EPS-Linares, Alfonso X El Sabio 28, Universidad de Jaén, E23700 Linares (Spain); <sup>C</sup>Conservation Department, Council of The Alhambra and Generalife, Granada, Spain.

\*mgcabrer@ujaen.es

**ABSTRACT:** The study of the pigments and degradation products of the decorative motifs painted on marble in the entrançy of the Room of the Ship located in the Palace of Comares in the Alhambra complex (Granada, Spain) has been approached using Raman spectrometry. The Alhambra, declared UNESCO World Heritage, is a monumental ensemble representative of the Moslem architecture and its wonderful decorations. It was a fortress, citadel and the palace area to give residence to the sultans of the Nasrid dynasty initially (XIII<sup>th</sup> century until Christian conquer) and to the Christian monarchy later (XV<sup>th</sup>+9<sup>th</sup> century). For this purpose, both in-situ analysis and subsequent analysis of samples in the laboratory to complete the results obtained in situ, have been performed, by using either a 785 nm excitation source with the portable Raman spectrometer and a 785 nm and 514 nm with the laboratory Raman instrument.

This study was performed during a cleaning intervention. The polychromy of the revetment appeared hidden by a dirty layer where calcite ( $\text{CaCO}_3$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) were identified during the in situ study. Only in some parts, characteristic Raman spectra of cinnabar ( $\text{HgS}$ ) was detected in dirty areas. In the clean areas spectral bands of cinnabar and also minium ( $\text{Pb}_3\text{O}_4$ ) frequently appeared mixed. Azurite ( $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ) and natural lapis lazuli, were identified in the blue decorations. Moreover, during the analysis in the laboratory, a degradation product as calcium oxalate ( $\text{CaC}_2\text{O}_4$ ) was found probably coming from the organic glues. However, the intense signals of both pigments and alteration products do not allow to appreciate the own bands of binders.

On the other hand, a study of the influence of the causes of aging and the nowadays cleaning procedure above the Raman spectrum of the polychromy was performed. For this, a simulation in a plaster support was carried out using the more common pigments and binders found in the Alhambra decorations. Different aging and cleaning process were applied and finally measured with Raman spectroscopy.

In conclusion, Raman spectroscopy has allowed a good identification of the pigments and degradation products even when the artistic piece is very dirty and aged or has been subjected to cleaning processes.

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## Partial Least Squares Calibration models toward the determination of the LOD in $^{90}\text{Zr}$ and $^{94}\text{Zr}$ generated by zirconium metallic particles on silica substrates via Laser Ablation Molecular Isotopic Spectroscopy (LAMIS)

C.D. Harris<sup>\*A</sup>, Codjo Akpovo<sup>A</sup>, Lewis E. Johnson<sup>A</sup>, Ashley C. Stowe<sup>B</sup>

<sup>A</sup>Department of Physics, Florida A&M University, Center for Plasma and Science Technology, Tallahassee, FL USA; <sup>B</sup>Y-12 National Security Complex, Oakridge, TN, USA.

\*Candace.harris@cepast.famu.edu

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*ABSTRACT: A calibration model in attempt to enhance LAMIS for its viable capabilities in sensitivity (down to ppm) and discrimination in isotopic analysis is presented here. The radiative transitions from molecular species along with the generated single shot spectra of zirconium particles ranging for 45-200  $\mu\text{m}$  in diameter was dispersed on the surface of a silica substrate were used as the predictors for the model. For the analyte(s) of interest, the generated plasma using a Q-switched 1064nm Nd:YAG excitation laser has been examined for their ZrO molecular bands. To ensure single particle spectra, the laser beam was focused to spot size of 100  $\mu\text{m}$  on the sample and a CCD system was employed for imaging single particle and laser interaction. A minimum of four band heads in the  $\alpha$ ,  $\beta$ ,  $\gamma$  and Ultraviolet system transitions have been identified. The data sets were analyzed using partial least squares regression (PLSR) in an effort to determine the isotopic ratios of  $^{94}\text{Zr}$  and  $^{90}\text{Zr}$  detected via LAMIS.*

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## Archaeological and Climatic data from elemental ratios using rapid analysis of shell carbonate with LIBS

Niklas Hausmann <sup>\*A</sup>, Panagiotis Siozos <sup>A</sup>, Demetrios Anglos <sup>A,B</sup>

<sup>A</sup>Institute of Electronic Structure and Laser, Foundation for Research and Technology – Hellas, Nik. Plast. 100, 70013 Heraklion, Greece; <sup>B</sup>Department of Chemistry, University of Crete, 70013 Heraklion, Greece.

\*niklas @iesl.forth.gr

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*ABSTRACT: The chemical composition of carbonate shell from palaeoecological and archaeological assemblages is laborious to analyse, yet the information that is locked within the tens of thousands of shell deposits worldwide contains valuable insights on past environments and human ecology. At present, studies struggle with the acquisition of sufficient amounts of data to make robust interpretations. Large amounts of information is inaccessible due to costly and time-intensive techniques, resulting in small, unrepresentative studies and a lack of comparability between them. Here we aim to develop the technique of Laser Induced Breakdown Spectroscopy (LIBS), which will allow rapid chemical analyses of carbonates, increasing the cost efficiency by a factor of 20, resulting in more comprehensive datasets. We apply the technique to various molluscan species around the world, to develop a rapid and affordable method and to globally advance the reconstruction of climate change, exploitation of coastal resources and human-landscape interactions. Similarly, the lower costs and higher speed of sample acquisition enables an extensive multi elemental analysis of shell structures of a larger set of mollusc specimens and may give insights into the mechanisms of shell carbonate precipitation.*

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## Methodological Effects in FTIR Spectroscopy: Implications for Structural Analyses of Biopolymers

Alexander A. Kamnev\*, Yulia A. Dyatlova, Anna V. Tugarova

Laboratory of Biochemistry, Institute of Biochemistry and Physiology of Plants and Microorganisms, Russian Academy of Sciences, 13 Prosp. Entuziastov, 410049, Saratov, Russia

\*aakamnev@ibppm.ru; a.a.kamnev@mail.ru

**ABSTRACT:** Fourier transform infrared (FTIR) spectroscopy in different methodological variants has been increasingly applied since its 'early days' up to now for structural molecular-level characterisation of diverse biological materials, from simple organic and biological molecules to biomacromolecular substances, biomaterials, cells and tissues. Structural characteristics of samples under study in FTIR spectra are provided by various vibrational modes related to virtually all functional groups of molecules, as well as to all inter- and intramolecular interactions which noticeably modify bond lengths and/or energies.

One of the conventional methodologies in FTIR spectroscopy, which has been used since early days of the technique, involves grinding and/or pressing a small amount of a dry solid sample with powdered IR-transparent materials such as halide salts, with KBr being the most widely used. However, it might be expected (as has been mentioned in some experimental reports; see, e.g. [1,2] and references reported therein) that the highly polar halide-salt matrix, when used for pressing the powdered sample under study in a pellet for FTIR spectroscopic measurements, could affect the state of polar moieties and systems of H-bonds (which often determine the structure, properties and biological functions of native biomacromolecules), leading to a slight but noticeable FTIR band shift (even for intramolecular H-bonds).

In this work, in order to address this methodological problem related to biological samples, a set of experimental data obtained by FTIR spectroscopy (involving the use of samples pressed with KBr or NaCl, i.e. in polar halide matrices) and by transmission FTIR or diffuse reflectance infrared Fourier transform (DRIFT) spectroscopic methodologies (involving measurements of thin films or pure powdered samples, respectively) were compared for several different biopolymers. The samples under study included: poly-3-hydroxybutyrate (PHB), a reserve biopolyester accumulated by bacteria as intracellular granules under unfavourable conditions (isolated from cell biomass of the rhizobacterium *Azospirillum brasilense*); dry PHB-containing bacterial biomass; pectin (plant carboxypolysaccharide obtained from apple peel) and its chemically modified derivative obtained by partial esterification of its galacturonide-chain hydroxyl moieties with palmitic acid [1]. Significant shifts of some FTIR vibrational bands related to polar functional groups of all the biopolymers under study, induced by the halide matrices used for preparing the samples for spectroscopic measurements (as compared to FTIR or DRIFT measurements without using KBr), were detected in FTIR spectra. The results obtained have important implications for correct structural analyses of polar or amphiphilic biopolymers using different methodologies of FTIR spectroscopy.

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## LA-ICP-MS examination of mummy hair strands from the archeological artifacts found in the Dominican Church in Vác, Hungary

János Balázs <sup>A</sup>, György Pálfi <sup>A</sup>, Ildikó Szikossy <sup>B</sup>, Ádám Braun <sup>C</sup>, Albert Kéri <sup>D</sup>, Gábor Galbács <sup>D\*</sup>

<sup>A</sup> Department of Biological Anthropology, University of Szeged, Szeged, Hungary; <sup>B</sup> Department of Anthropology, Hungarian Natural History Museum, Budapest, Hungary; <sup>C</sup> Hertelendi Laboratory of Environmental Studies, ATOMKI, Debrecen, Hungary; <sup>D</sup> Department of Inorganic and Analytical Chemistry, University of Szeged, Hungary.

\*galbx@chem.u-szeged.hu

**ABSTRACT:** In 1994, a large set of anthropological artifacts of great international significance was discovered in Vác, Hungary. A secret crypt, that had been bricked up for over 200 years, was found in the Dominican Church of the city. The set of artifacts includes 265 hand-painted coffins which contain bodies naturally mummified due to the temperature and aridity existing in the crypt. These mummies, as well as their accessories, were the subject of several anthropological investigations over the years [1, 2, 3].

The goal of the present study was to investigate the trace elemental distribution in hair strands from these mummies by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). Such chemical anthropological studies can provide information about the living conditions, dietary intakes, medical treatments, etc. of the mummified persons. This is the first such research on this set of artifacts. The analysis was carried out by using an Agilent 8800x triple quad ICP-MS spectrometer coupled to an ESI-NWR laser ablation unit operating at 213 nm wavelength. Measurements with lateral and depth resolution were conducted on six samples. The distribution of Cu, Zn, Sr, Hg, Pb, Al, Fe, As and Ag elements were studied. The average concentrations in the samples were also assessed after solid calibration using a recent hair sample, the elemental composition of which was determined by solution-mode ICP-MS analysis following acid digestion.

In our contribution, we discuss the problems associated with sample preparation and the optimization of measurement conditions, and we also give a paleopathological and chemical anthropological evaluation of the results based on available historical data on the mummified persons as well by a comparison with literature data.

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## Research of Islamic Enamel Glass from Excavations at Bolgar Settlement (Russia)

Rezida Khamchenkova<sup>A,B</sup>, Airat Gubaidullin<sup>A</sup>, Rafind Sharifullin<sup>A</sup>, Eugeny Nujdin<sup>C</sup>

<sup>A</sup> Restoration & Analytical Department, Institute of Archaeology, Tatarstan Academy of Sciences, Kazan, Russian Federation; <sup>B</sup>Centre of Excellence "Archaeometry", Kazan Federal University, Kazan, Russian Federation; <sup>C</sup> Laboratory of electronic microscopy, Kazan National Research Technical University - KAI, Kazan, Russian Federation.

\* rkhamch@gmail.com

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**ABSTRACT:** Archaeological finds of enamel glass dated 13-14 centuries were studied by scanning electron microscopy and emission spectral analysis. Chemical structure showed that the glass was produced on sodium ash. Analytical data showed differences of enamel coloring reagents. The comparative analysis allowed to determine the production places of certain artifacts.

A special place in the diverse material discovered at excavations in Volga Bulgaria settlements belongs to glass findings demonstrating a high level of population's welfare. This work is dedicated to the research of fragments made of various enamel glass originating from the archaeological material of Bolgar settlement dating back to the period of the Golden Horde.

The chemical composition of the artifacts was researched using two independent methods – scanning electron microscopy (SEM) and emission spectral analysis (ESA). The works were conducted using Axio Observer Z1 and Axio Imager Z2m AURIGA CrossBeam with an Inca X-Max energy-dispersion spectrometer and a DFS-458 diffraction spectrograph. All fragments were crafted using glass with high sodium content - the so-called "Islamic" glass. SEM research of the enamel allowed to identify the dyes used by the glassmakers. The red enamel was obtained by adding hematite to the glass, the yellow colour is attributable to the lead and tin component, and the green enamel was obtained by applying copper on a lead base. The blue enamel discovered on glass fragments features various compositions.

As is known, the main centers of Islamic enamel glass production were in Syria and Egypt. A comparative analysis of formulation characteristics was conducted on the basis of ESA results, and potential sources of imported glass were determined. One of the fragments is most likely a Venetian forgery dating back to the 14th century.

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## Evaluation of ensemble classification methods in laser-induced breakdown spectroscopy measurements

Jakub Klus<sup>\*A, B, C</sup>, Pavel Pořízka<sup>A, C</sup>, David Prochazka<sup>A, C</sup>, Jan Novotný<sup>A, B, C</sup>, Karel Novotný<sup>C</sup>, Aleš Hrdlička<sup>C</sup>, Jozef Kaiser<sup>A, B, C</sup>

<sup>A</sup>Materials Characterization and Advanced Coatings, Central European Institute of Technology, Purkyňova 656/123 Brno, Czech Republic; <sup>B</sup>Institute of Physical Engineering, Brno University of Technology, Technická 2 Brno, Czech Republic; <sup>C</sup>AtomTrace a. s., Kolejní 9 Brno, Czech Republic.

\*jakub.klus@ceitec.vutbr.cz

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*ABSTRACT: Complex information hidden in the atomic emission spectrum of ores and other samples can be viewed from many angles. Current progress in information theory and statistics enables us to automatically detect and classify differences and similarities within measurements. With rising availability of different classifiers (both supervised and unsupervised), one is challenged with the possibility of combining their outputs. Such a methodology is called ensemble classification and there are few known possibilities of solving this phenomenon. One example for all is voting classification, where each classifier has a single vote and resulting number of votes determines the class.*

*A study on line assignment in spectra retrieved by means of Laser-Induced Breakdown Spectroscopy in the scope of ensemble classification is addressed in this work. For each emission line in a single spectrum, a set of simple classifiers describing the probability of element presence was created. Results of these classifiers are then combined and evaluated by different methods of ensemble classification. To improve the ensemble classification other techniques such as weighting of classifier outputs or backward feature selection will be applied. The result of this method will yield in an autonomous probabilistic assignment of elements to spectral lines in detected LIBS spectrum.*

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## Simulation of Artefacts in X-ray Florescence Microscopy Based on Sample Topography

Fulvio Billè <sup>A</sup>, George Kourousias\* <sup>A</sup>, Alessandra Gianoncelli <sup>A</sup>

<sup>A</sup> Elettra-Sincrotrone Trieste, Basovizza, Trieste, Italy

\*george.kourousias@elettra.eu

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*ABSTRACT: For a wide range of applications, X-ray Florescence (XRF) spectroscopy is the main non-destructive technique for elemental analysis. The angular dependence of XRF is known [1] and can provide additional information [2] but in certain cases it can yield artefacts due to the topology of the sample especially in experimental setups that use X-ray micro- or nano-probes. On a recent work the authors studied XRF microscopy artefacts in elemental maps of topologically complex samples [3]. For the observations and the development of a map correction technique, a method for simulating those artefacts has been developed. In this work the latest version of the artefact simulation method will be presented and a series of topologies and their corresponding artefacts will be shown. This should assist in the systematic development of new artefact correction methods but also for hinting on where such artefacts may be present in existing XRF maps. The latter is often prevalent in cell imaging but in general any microscopy mapping of topographically pronounced samples is prone to exhibit artefacts.*

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## Characterization of pigment compositions by LIBS beyond limits of XRF and PIXE techniques

Violeta Lazic, Roberta Fantoni, Monia Vadrucci

ENEA, Dep. FSN-TECFIS-DIM, Via E. Fermi 45, 00044 Frascati (Italy)

\*violeta.lazic@enea.it

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*ABSTRACT: We performed stratigraphic LIBS measurements on different historically used pigments, previously characterized by XRF and PIXE instruments. A single laser shot delivered to the target allows recognizing od cinnabar, ochre, azurite and lazurite, and detecting of minor pigment constituents or impurities, not observed by the previous two techniques. In particular, XRF was not able to detect lazurite while by LIBS it was possible also to distinguish the same over-layered by azurite and to find their relative in-depth distribution. Here we discuss the comparative measurements by the three techniques applied also on other materials related to Cultural Heritage.*

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## Multielemental mapping by scanning synchrotron x-ray fluorescence in tumor human cells prostatic supplemented with zinc.

Karolynne M. J. Rocha<sup>A</sup>, Roberta G. Leitão<sup>\*B</sup>, Eliane G. Oliveira Barros<sup>C</sup>, Maria Aparecida Oliveira<sup>C</sup>,  
Catarine G. L. Canellas<sup>B</sup>, Marcelino J. Anjos<sup>A, B</sup>, Luiz E. Nasciutti<sup>C</sup>, Ricardo T. Lopes<sup>A</sup>

<sup>A</sup>Nuclear Instrumentation Laboratory, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil; <sup>B</sup>Physics Institute, Stated University of Rio de Janeiro, RJ, Brazil; <sup>C</sup>Biomedical Sciences, Federal University of Rio de Janeiro, RJ, Brazil.

\*roberta.leitao@uerj.br

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**ABSTRACT:** Prostate cancer continues to be one of the most common fatal cancers in men. Zinc is an essential trace element, critical for diverse biological functions in the human body. The main function of the prostate is the high production and secretion of citrate which is possible due to the unique accumulation of zinc by prostatic epithelial cells. In relation to prostate cancer, it can inhibit the growth of tumor cells, due to the stop of cell cycle and / or induction of apoptosis. The X-ray microfluorescence technique ( $\mu$ XRF) is a rapid and non-destructive method of elemental analysis that provides useful elemental information about samples without causing damage or requiring extra sample preparations. This study investigated the behavior of cells in spheroids of human prostate cells, tumor cell line androgen independent (DU145) and tumor cell line androgen dependent (LNCaP), after supplementation with zinc chloride by 24 hours and 48 hours using synchrotron X-ray microfluorescence ( $\mu$ SRXRF) and analyzed cell viability through colorimetric cytotoxicity assay (MTT). The measurements were performed with a standard geometry of 45° of incidence, excited by a white beam using a pixel of 25  $\mu$ m and a time of 300 ms/pixel at the XRF beamline at the Synchrotron Light National Laboratory (Campinas, Brazil). The results by SR $\mu$ XRF showed non-uniform Zn distribution in all the spheroids analyzed. It was possible observed that Zn intensity were changed with the Zn supplementation. These results suggest that Zinc may affect cell growth and/or cell death. Therefore, the Zn supplementation changes the metabolic of prostate cancer cell.

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## Study of elemental distribution in human prostatic carcinoma cell spheroid culture using synchrotron radiation based x-ray fluorescence.

Karolynne M. J. Rocha<sup>A</sup>, Roberta G. Leitão<sup>\*B</sup>, E.G.Oliveira-Barros<sup>C</sup>, Maria Aparecida Oliveira<sup>C</sup>,  
Catarine G. L. Canellas<sup>B</sup>, Marcelino J. Anjos<sup>A, B</sup>, Luiz E. Nasciutti<sup>C</sup>, Ricardo T. Lopes<sup>A</sup>

<sup>A</sup>Nuclear Instrumentation Laboratory, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil; <sup>B</sup>Physics Institute, Stated University of Rio de Janeiro, RJ, Brazil; <sup>C</sup>Biomedical Sciences, Federal University of Rio de Janeiro, RJ, Brazil.

\*nome.cognome@university.xy

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**ABSTRACT:** Cancer is a worldwide public health problem and prostate cancer continues to be one of the most common fatal cancers in men. The X-ray microfluorescence technique ( $\mu$ XRF) is a rapid and non-destructive method of elemental analysis that provides useful elemental information about samples without causing damage or requiring extra sample preparations. This study investigated the behavior of cells in spheroids of human prostate cells, tumor cell line (DU145) and normal cell line (RWPE-1), after supplementation with zinc chloride by 24 hours and 48 hours using synchrotron X-ray microfluorescence ( $\mu$ SRXRF) and analyzed cell viability through colorimetric cytotoxicity assay (MTT). The measurements were performed with a standard geometry of 45° of incidence, excited by a white beam using a pixel of 25  $\mu$ m and a time of 300 ms/pixel at the XRF beamline at the Synchrotron Light National Laboratory (Campinas, Brazil). The results by SR $\mu$ XRF showed non-uniform Cu, Fe and Zn distributions in all the spheroids analyzed. It was possible observed that intensities of Cu, Fe and Zn were changed with the Zn supplementation. MTT assay's results were not significant, which indicates that the cell viability was not changed.

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## Biospecific Metabolism Based and Click Chemistry Mediated Europium Tagging Enable the Determination of D-Alanine Density of Bacterial Cell Wall Peptidoglycan Layers Using ICP-MS

Yong Liang<sup>A</sup>, Qiuquan Wang<sup>\*A,B</sup>

<sup>A</sup> Department of Chemistry & the MOE Key Lab of Spectrochemical Analysis and Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China; <sup>B</sup> State Key Lab of Marine Environmental Science, Xiamen University, Xiamen 361005, China.

[\\*yongliang@stu.xmu.edu.cn](mailto:*yongliang@stu.xmu.edu.cn)

**ABSTRACT:** The importance of D-Alanine (D-Ala) in building bacterial cell wall peptidoglycan (PG) network has been known for decades<sup>[1]</sup>, but the number of D-Ala ( $n_{D-Ala}$ ) in the PG layers was hard to determine using the currently available methods<sup>[2]</sup>, limiting more intensive investigation of the bacterial cell wall composition and structure and corresponding biophysical and chemical properties as well. We are able not only to quantify  $n_{D-Ala}$  and count the bacterial number ( $n_{bacterium}$ ) as exemplified by the two typical Gram-negative (*E. coli*) and Gram-positive (*S. aureus*) bacteria as low as 76 *S. aureus* and 225 *E. coli*, but also to determine the “density” of D-Ala ( $d_{D-Ala} = n_{D-Ala}/n_{bacterium}$ ) in the PG layers of *E. coli* ( $(1.41 \pm 0.02) \times 10^{-18}$  mol/bacterium) and *S. aureus* ( $(2.05 \pm 0.02) \times 10^{-18}$  mol/bacterium) using ICP-MS based on bacterium-exclusive metabolism of alkyne-D-Ala and click chemistry mediated europium tagging strategy. Results obtained from studying the change of  $d_{D-Ala}$  during bacterial growth and under the attack of antibiotics suggested that  $d_{D-Ala}$  is an intrinsic index of a certain bacterial species. It reflects the crosslinking level of the PG layers, governing not only the status of the bacterial growth accompanying PG synthesis and remodeling but also the defending ability against the attack from different drugs with similar bacteria-killing mechanism.

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## On-sorbent derivatization of carbonyl compounds in exhaled breath

Tommaso Lomonaco <sup>\*A</sup>, Andrea Romani <sup>A</sup>, Silvia Ghimenti <sup>A</sup>, Massimo Onor <sup>B</sup>, Denise Biagini <sup>A</sup>, Francesca G. Bellagambi <sup>A</sup>, Fabio Di Francesco <sup>A</sup>, Roger Fuoco <sup>A</sup>

<sup>A</sup> Dipartimento di Chimica, Università di Pisa, Via Giuseppe Moruzzi 13, 56124 Pisa, Italy; <sup>B</sup> Istituto di Chimica dei Composti Organometallici, Consiglio Nazionale delle Ricerche, Via Giuseppe Moruzzi 1, 56124 Pisa, Italy.

\*tommaso.lomonaco@unipi.it

**ABSTRACT:** Over the last few years, breath analysis for monitoring metabolic disorders caused by specific diseases (e.g. heart failure) has become more and more attractive due to its non-invasiveness. Various classes of volatile organic compounds (VOCs) can be measured in exhaled breath, including the oxygen-containing substances (e.g. aldehydes and ketones) formed during the fatty acid lipid peroxidation of cell membranes. Among these, aldehydes are particularly difficult to monitor in exhaled breath since they are reactive compounds and tend to decompose or react during sample preparation or storage. In addition, analytical problems occur from their low concentrations in exhaled breath. Therefore, chemical derivatization ideally coupled with pre-concentration techniques may offer a solution to overcome these problems. Aim of this work was to develop an analytical procedure including on-sorbent derivatization technique and thermal desorption coupled to GC-MS/MS. Carbonyls in standard gaseous mixtures and/or breath samples were collected onto O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA)-coated Tenax GR sorbent packed in a stainless-steel tube. A mixture of carbonyl compounds, composed by linear aldehydes (C2-C9) and linear ketones (C3-C9), were used to optimize the analytical performances of on-sorbent technique. Pre-coated sorbent tubes were thermally desorbed by a TD-100 multi-tubes auto-sampler (Markes International) and PFBHA-oximes were analysed by a 7890B GC System equipped with a DB5ms gas chromatographic column (60 m, 0.25 mm ID, 1.0 µm) and coupled to a 7010 MS Triple Quad mass spectrometer (Agilent Technologies). The effect of temperature and reaction time as well as the amount of PFBHA spiked into Tenax GR sorbent tubes was evaluated using a 2<sup>3</sup> full factorial design. In addition, the influence of humidity level and sampling flow rate on the collection efficiency of carbonyl into pre-coated sorbent tubes was assessed. Under optimized derivatization, extraction, and analysis conditions the method allows to successfully determine carbonyl analytes in breath. A quantitative linear response in the range 0.1-20 ppbv, detection limits close to 50 pptv and no carry-over effect were observed. The method was used in the framework of the H2020 HEARTEN project to monitor breath composition of patients suffering from heart failure.

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## Structure–Spectra Correlations in Anilate Complexes with Picolines

Katarzyna Łuczyńska<sup>\*A,B</sup>, Kacper Drużbicki<sup>B,C</sup>, Krzysztof Lyczko<sup>A</sup>, Jan. Cz. Dobrowolski<sup>A,D</sup>

<sup>A</sup> Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland; <sup>B</sup> Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, 141980 Dubna, Russia; <sup>C</sup> Department of Radiospectroscopy, Faculty of Physics, Adam Mickiewicz University, Umultowska 85, 61-614, Poznan, Poland; <sup>D</sup> National Medicines Institute, 30/34 Chełmska Street, 00-725 Warsaw, Poland.

\* k.luczynska@ichtj.waw.pl

**ABSTRACT:** In the era of rapid progress in supramolecular chemistry, low-weight organic molecular crystals have attracted much attention in the design of new functional materials, where donor-acceptor type molecular complexes are particularly interesting. There is a particular interest in complexes of organic aromatic acids with heterocyclic aromatic amines, from which the family of anilic acids (2,5-dihalo-1,4-benzoquinone; hereafter XA) was found to be of vital importance. Anilic acids have been used in combination with various secondary molecular components to produce chains, sheets, and three dimensional structures with a reasonable degree of design intent. Here, we report a joint structural and spectroscopic study of a series of hydrogen-bonded chloranilate and bromanilate complexes with  $\alpha$ - and  $\beta$ -picolines. Single-crystal structures at 100 K are provided for all the systems analyzed, which were found to form B:XA:XA:B, (B:XA:B):XA, and B:XA:B type synthons, where XA and B stand for the acid and base molecules, respectively. The intermolecular forces driving the crystal structures were analyzed both qualitatively and quantitatively with the help of reduced density gradient and PIXEL approaches. By extending single-crystal X-ray crystallography onto computationally supported high-resolution solid-state spectroscopy, we provide a comprehensive analysis of spectral signatures that can possibly facilitate the design and recognition of the supramolecular architectures formed by these kinds of synthons. To this end, we employed nuclear magnetic resonance spectroscopy along with complementary optical (infrared, Raman, terahertz time-domain spectroscopy) and neutron (inelastic neutron scattering) vibrational techniques. Despite a large chemical similarity, the studied systems exhibited strikingly different spectral responses. Based on state-of-the-art first-principles calculations for solid-state, in both static and time-evolved manners, the spectral influences of long-range dipole coupling, proton transfer, symmetry-distortion, as well as anharmonicity are covered extensively. In this way, we take the necessary first step needed to gather combined structure–spectroscopy data on low-weight supramolecular synthons, which are important in crystal engineering and materials science.

## Determination of As in complex samples using solid sampling high-resolution continuum source graphite furnace atomic absorption spectroscopy.

Raquel C Machado<sup>\*A,B,D</sup>, Maite Aramendia<sup>B,C</sup>, Ana Rita A. Nogueira<sup>D</sup>, Martin Resano<sup>B</sup>

<sup>A</sup>Department of Chemistry, Federal University of São Carlos, São Carlos, SP, Brazil; <sup>B</sup>Department of Analytical Chemistry, University of Zaragoza, Zaragoza, Spain; <sup>C</sup>Centro Universitario de la Defensa-Academia General Militar de Zaragoza, Zaragoza, Spain; <sup>D</sup>Embrapa Pecuária Sudeste, São Carlos, SP, Brazil

\*raquelcm.quim@gmail.com

**ABSTRACT:** The monitoring of As in several kinds of solid samples is carried out by government agencies in different countries, which set tolerable limits for this contaminant due to its known toxicity. Several analytical methods have been reported to determine this analyte using different techniques, such as inductively coupled plasma optical emission spectrometry (ICP OES), inductively coupled plasma mass spectrometry (ICP-MS), hydride generation atomic absorption spectrometry (HG AAS) and graphite furnace atomic absorption spectrometry (GF AAS).<sup>1</sup> However, As determination by any of these methods is not a trivial task due to different reasons, such as the location of the As resonance lines in the UV region, high ionization potential for this element or influence of severe spectral interferences compromising accuracy. The problem becomes even more serious when solid samples are to be analyzed, which often require extensive sample pre-treatments implying risks of analyte losses, contamination or degradation of detection limits. In this context, development of analytical methods allowing for the direct determination of As in solid samples is an interesting alternative for overcoming these problems.<sup>2,3</sup> The use of high-resolution continuum source (HR CS) GF AAS seems to be especially well suited for this application, due to its unique features including a Xe light source providing high intensity in the UV range and its capability for carrying efficient correction of spectral overlaps, which is crucial at this particularly difficult region of the spectrum.<sup>2,4</sup> In this contribution, an analytical method for the determination of As in complex samples is presented, using HR-CS GF AAS with direct solid sampling. All aspects of method development such as selection of a proper chemical modifier, optimization of the temperature program and strategies to correct for spectral overlaps will be critically discussed.

The authors are grateful to São Paulo Research Foundation (2013/26672-5, 2016/07749-5 and 2015/14488-0), and to Conselho Nacional de Desenvolvimento Tecnológico e Científico (307639/2014-2) for fellowships and financial support. The authors also acknowledge the funding from CTQ2015-64684-P (MINECO/FEDER) and the Aragon Government (Fondo Europeo de Desarrollo Regional).

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## On the possibilities of Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) for the determination of heavy metal contamination of osteological remains and ceramics – an archaeometric study

Ana Manhita<sup>\*A</sup>, Pedro Barrulas<sup>A</sup>, Maria da Conceição Lopes<sup>B</sup>, Frank Vanhaecke<sup>C</sup>,  
Cristina Barrocas Dias<sup>D</sup>

<sup>A</sup>Laboratório HERCULES, Universidade de Évora, Évora, Portugal; <sup>B</sup>Centro de Estudos de Arqueologia, Artes e Ciências do Património and Departamento de História, Estudos Europeus, Arqueologia e Artes, Universidade de Coimbra, Coimbra, Portugal; <sup>C</sup>Department of Analytical Chemistry, Ghent University, Ghent, Belgium;

<sup>D</sup>Laboratório HERCULES and Departamento de Química, Escola de Ciências e Tecnologia, Universidade de Évora, Évora, Portugal.

\*anaccm@uevora.pt

**ABSTRACT:** The archaeological sites of São Cucufate and Monte da Cegonha, located in the municipality of Vidigueira, South Portugal, show Roman occupation from the 1<sup>st</sup> century AD to the 4<sup>th</sup> century AD. Both villae were agricultural centres during Roman occupation. The archaeological finds collected during the 1970's and 1980's campaigns include osteological remains and a wide pottery collection, which includes common ceramics, amphorae and other containers.

Determination of trace elements in archaeological ceramics and bones, using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), can assist in the reconstruction of paleodiet and also help to obtain information on the individual's contamination by heavy metals. For example, skeletal lead content indicates lifetime lead ingestion and can be related with individuals' dietary habits. Laser ablation-ICP-MS (LA-ICP-MS) is a highly sensitive microprobe technique with many potential applications in chemistry-based archaeological research. By controlling wavelength and pulse length of the laser, it is possible to remove micro-samples from a surface at different levels of depth [1]. LA-ICP-MS was used to check if there is a lead enrichment on the inside of Roman wine amphorae, which may have been in contact with contaminated products. The technique was also applied to osteological remains, to check for differences on the intake of heavy metals. Acknowledgements: Ana Manhita acknowledges Fundação para a Ciência e Tecnologia for a Post-Doctoral fellowship (Ref. SFRH/BPD/108717/2015) within the context of POCH – Programa Operacional Capital Humano, co-financed by Fundo Social Europeu and national funding of the MCTES – Ministério da Ciência, Tecnologia e Ensino Superior.

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## In situ analysis of paper documents using portable EDXRF setup with triaxial geometry

Sofia Pessanha<sup>A</sup>, Jorge M. Sampaio<sup>B</sup>, Maria Luisa Carvalho<sup>A</sup>, Marta Manso<sup>A\*</sup>

<sup>A</sup>LIBPhys – UNL- Laboratório de Instrumentação, Engenharia Biomédica e Física da Radiação, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

<sup>B</sup>LIP – Laboratório de Instrumentação e Física Experimental de Partículas, Av. Elias Garcia 14 1º D, 1000-149 Lisboa, Portugal

\*marta.sampaio@fct.unl.pt

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**ABSTRACT:** In this work we present the in situ analysis of documents belonging to the collection of Biblioteca Nacional de Portugal for paper characterization. A quantitative methodology will be presented based on the paper standards composition. X-ray fluorescence (XRF) spectroscopy is a powerful analytical tool with a broad range of applications and has proven to be extremely useful in the analysis of artworks and archaeometry studies. The setup used in this work consists of a portable equipment with triaxial geometry between the X-ray tube, the secondary target, the sample and the detector. This geometry reduces significantly the Bremsstrahlung background, produced in the X-ray tube, through crossed polarization in the secondary target and in the sample. In this way, a better peak-to-background ratio is obtained, improving the detection limits and leading to higher sensitivity. This setup reveals great improvements in the analysis of trace elements in low-Z matrix samples, namely manuscripts and paper artworks.

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## Multi-analytical study of foxing stains on paper

M. Nunes<sup>A</sup>, C. Relvas<sup>A</sup>, M. Manso<sup>B,C</sup>, M. L. Carvalho<sup>B,D</sup>, P. Barrulas<sup>A</sup>, C. Miguel<sup>A</sup>, A.T. Caldeira<sup>A,E</sup>,  
F. Figueira<sup>F</sup>, T. Ferreira<sup>\*A,E</sup>

<sup>A</sup>HERCULES Laboratory, University of Évora, Largo Marquês de Marialva, 8, 7000-609 Évora, Portugal;

<sup>B</sup>LIBPhys-UNL, Laboratório de Instrumentação, Engenharia Biomédica e Física da Radiação, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516, Caparica, Portugal;

<sup>C</sup>Faculdade de Belas-Artes da Universidade de Lisboa, Largo da Academia Nacional de Belas-Artes, 1249-058 Lisboa, Portugal;

<sup>D</sup>Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica, Portugal;

<sup>E</sup>Chemistry Department at the Science and Technology School, University of Évora, Rua Romão Ramalho, 59, 7000-671 Évora, Portugal;

<sup>F</sup>José Figueiredo Laboratory, General Directorate for Cultural Heritage, 1249-018 Lisbon, Portugal.

*\*tasf@uevora.pt* Paper based materials are part of the cultural heritage of a nation as a living memory of our past. Cellulose degradation phenomena weaken and discolorate paper over time [1]. Paper documents can be compromised by chemical, physical and biological deterioration that can culminate in the appearance of foxing. Foxing spots are stains of reddish-brown, brown or yellowish color, generally of small dimensions, with sharp or irregular edges, many of which, when excited with UV light, show fluorescence [2]. Several factors are presumably involved in this form of paper deterioration, such as, chemical degradation as acid hydrolysis or autoxidation of cellulose due to the presence of metal ions and moisture content, relative humidity and surrounding environment as well as microbiological contamination caused by fungi and bacteria under certain conditions [3-5]. This study aims to contribute to the understanding of the abiotic and biotic causes of this phenomenon and also characterize it from a chemical and morphological point of view. To achieve this, a multi-analytical approach was used. The papers under study, from 18<sup>th</sup> and the 20<sup>th</sup> centuries, exhibit different types of foxing stains. Some stains are multiple small of grey/brown tone while others present higher dimensions or diffuse irregular shape and size. Photographic imaging under different illuminations, namely standard, raking and transmitted lights, and UV radiation for fluorescence detection, and optical microscopy were used to evaluate the tones of paper samples and stains and paper topography. Foxed and unfoxed areas were also analyzed by vibrational spectroscopy using micro-Fourier transform infrared spectroscopy in the attenuated total reflection mode to obtain distribution profiles of compositional and degradation products. The use of micro-X-ray diffraction allowed to investigate the crystalline fillers used in the paper production. Elemental composition from fillers and contaminations and fibers' morphology were evaluated by variable pressure scanning electron microscopy coupled with energy dispersive X-ray spectroscopy. Elemental mapping obtained by micro-X-ray fluorescence spectrometry was carried out to identify any possible metal contamination on the stains and surrounding areas. Evaluation of metallic elements distribution namely, iron and copper, was done by laser ablation inductively coupled plasma mass spectrometry. Microbiological studies were carried out in order to evaluate the influence of biotic attack in the foxed papers. [1] C. Corsaro, D. Mallamace, J. Lojewska, F. Mallamace, L. Pietronero, M. Messori, *Scientific Reports* (3), 2013, 2896. [2] M. Bicchieri, S. Ronconi, F.P. Romano, L. Pappalardo, M. Corsi, G. Cristoforetti, S. Legnaioli, V. Palleschi, A. Salvetti, E. Tognoni, *Spectrochimica Acta Part B: Atomic Spectroscopy* (57) 7, 2002, 1235. [3] R. Buzio, P. Calvini, A. Ferroni, U. Valbusa, *Applied Physics A* (79), 2004, 383. [4] S. Manente, A. Micheluz, R. Ganzerla, G. Ravagnan, A. Gambaro, *International Biodeterioration & Biodegradation* (74), 2012, 99. [5] M. Manso, M. Costa, M. L. Carvalho, *Applied Physics A* (90), 2008, 43.



## LIBS-SSI-MS: Simultaneous elemental and molecular analysis of metal containing biomolecules

Konstantinos Marmatakis<sup>\*A,B</sup>, Spiros A. Pergantis<sup>A</sup>, Demetrios Anglos<sup>A,B</sup>

<sup>A</sup> Department of Chemistry, University of Crete, PO Box 2208, GR 710 03 Heraklion, Crete, Greece

<sup>B</sup> Institute of Electronic Structure and Laser, Foundation for Research and Technology - Hellas (IESL-FORTH), P.O Box 1385, GR 711 10 Heraklion, Crete, Greece

\* kmarm@iesl.forth.gr, chemp860@uoc.gr

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**ABSTRACT:** The integration of appropriate analytical techniques towards the development of hybrid instrumentation is of key importance for performing efficient speciation analysis. Several studies have shown that combination of separation techniques, such as high performance liquid chromatography, with atomic and molecular mass spectrometry enables speciation analysis of metal and metal containing biomolecules and complexes. However the simultaneous use of elemental mass spectrometry, for example, ICP-MS, along with molecular mass spectrometry is a highly non-trivial task. In this context, we are exploring an alternative approach that combines sonic-spray ionization (SSI) mass spectrometry (MS), a well-advanced molecular analysis technique, with laser induced breakdown spectroscopy (LIBS), a fast and straightforward tool for elemental analysis. The analysis is performed in an aerosol spray produced by use of a pneumatic nebulizer. The aerosol, typically produced from a water-methanol solution containing various types of metal complexes and metalloproteins, is fed into the inlet of the mass spectrometer at a constant flow, 15-20  $\mu\text{L}/\text{min}$ , and mass spectra are collected. The spray is being simultaneously interrogated, at a repetition rate of 5-10 Hz, by pulses from a nanosecond laser (Nd:YAG,  $\lambda = 1064 \text{ nm}$ ) that give rise to the formation of strongly emitting plasma, off of which time-resolved LIBS spectra are recorded. Spatial constraints are dealt with by a custom designed, compact optical setup, which enables tight focusing of the laser beam in the space between the nebulizer tip and the MS inlet along with efficient collection of the plasma plume emission. In the present study we describe the integration of the SSI-MS with LIBS into a hybrid system, explain certain key technical aspects and present recent results from the simultaneous analysis of a number of metal containing complexes and biomolecules. It is shown that the ablation process has some, but clearly not significant interference, with the molecular MS measurements in metal proteins. The potential for coupling the hybrid LIBS-SSI-MS analysis directly with a HPLC is being investigated and preliminary results are shown.

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## Laser Induced Breakdown Spectroscopy applied to the evaluation of nanoparticles treatments on limestones.

Maripaz Mateo<sup>\*A</sup>, Javier Becerra<sup>B</sup>, Ana Paula Zaderenko<sup>B</sup>, Pilar Ortiz<sup>B</sup>, Gines Nicolas<sup>A</sup>

<sup>A</sup> Departamento de Ingeniería Industrial II, Laser Applications Laboratory, Universidade da Coruña, C/Mendizabal s/n, 15403 Ferrol, Spain;

<sup>B</sup> Departamento de Sistemas Fisicos, Quimicos y Naturales, Universidad Pablo de Olavide, ES-41013, Seville, Spain.

\*paz.mateo@udc.es

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*ABSTRACT: In this work, laser-induced breakdown spectroscopy (LIBS) has been used for the in-depth characterization of new nanocomposites to be employed in heritage buildings for protective purposes. In particular, limestones treated with silver nanoparticles or with silver/titanium dioxide/charcoal activated nanocomposites have been analyzed. These nanomaterials are known to be an effective protection against bacteria development but their assessment depends on the in-depth penetration of the compound. For this reason, it is of great interest to characterize the location of these nanomaterials in the matrix with the aim of controlling the treatment process. This characterization has been successfully performed by LIBS depth-profiling. In this research, two biocidal treatments based on two nanocomposites with silver and silver/titanium dioxide/charcoal activated synthesized by a bottom-up method with sodium borohydride as reduction agent have been tested on limestones from Utrera's quarry (Seville, Spain). This stone was employed in historical buildings in the south of Spain, such as Cathedral and Town hall in Seville or Cathedral in Cádiz. The results of the analysis of these samples demonstrate the capability of LIBS technique for the detection of nanocomposites and for the generation of depth profiles and its potential for the analysis of the nanoparticles diffusion in the matrix after protective treatments of structural materials employed in historical buildings.*

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## **Laser-induced breakdown spectroscopy analysis of Titanium-Niobium coatings generated by laser cladding for its potential use in orthopedic implants**

Maripaz Mateo\*, Jose Manuel Amado, Maria Jose Tobar, Armando Yañez, Gines Nicolas

Departamento de Ingeniería Industrial II, Laser Applications Laboratory, Universidade da Coruña, C/Mendizabal s/n, 15403 Ferrol, Spain.

\* paz.mateo@udc.es

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*ABSTRACT: The development of new alloys is crucial for long-term stability of artificial joints in implant-supported prosthesis. The titanium–niobium alloy has superior corrosion resistance than pure titanium and an elastic modulus that is close to the bones, which solves the problem of stress shielding. Therefore, that alloy can be used as a biomedical material for orthopedic applications. By laser cladding technique it is possible to generate a coating of Ti-Nb alloy on the surface of a titanium substrate in order to enhance its biocompatibility for prosthetic purposes. However, the process parameters need to be optimized and different proportions of Ti and Nb have to be tested in order to generate a clad with a good quality, mechanical properties and biological behavior. In a recent paper, we have demonstrated the capability of laser-induced breakdown spectroscopy (LIBS) technique for the chemical analysis of clad layers composed by mixtures of WC ceramics with NiCrBSi alloys and generated by laser cladding. In this work, LIBS technique will be used to determine the composition of laser clads of Ti and Nb alloys deposited in different proportions on Ti and Ti6Al4V alloy substrates. The objective of the analysis is to compare the final and the theoretical composition of the clads, estimated from the composition of the feedstock powdered material, in order to control the laser cladding process. For that purpose, sintered samples with different proportion of Nb and Ti will be also analyzed and used as standards for generating calibration curves. In addition, compositional rasters and maps will be generated by LIBS in the cross section of the clads to study the homogeneity of the coating and the possible dilution with the substrate.*

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## Effect of Gypsum on Sulfur Isotope Ratio of Vermilion Painted on Gypsum Wall

Takeshi Minami<sup>\*A</sup>, Evanthia Tsantini<sup>B</sup>, Kazuya Takahashi<sup>C</sup>

<sup>A</sup> School of Sci. & Engineer., Kindai Univ., 3-4-1 Kowakae, Higashiosaka, Osaka 577-8502 Japan; <sup>B</sup> Equip de Recerca Arqueològica i Arqueomètrica, Universitat de Barcelona (ERAAUB), Departament de Prehistòria, Història Antiga i Arqueologia, Montalegre, 6-8, 08001 Barcelona, Spain. <sup>C</sup> RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan.

\*minamita@life.kindai.ac.jp

**ABSTRACT:** Vermilion is a crushed cinnabar mineral that provides brilliant red color. It was used as a red pigment for the decoration of wall paintings from the Prehistory. The chemical composition of vermilion is mercury sulfide, and sulfur has four stable isotopes:  $^{32}\text{S}$ ,  $^{33}\text{S}$ ,  $^{34}\text{S}$ , and  $^{36}\text{S}$ . Sulfur isotope analysis is the method that calculates the ratio of  $^{34}\text{S}/^{32}\text{S}$ . It has been reported, experimentally, that the  $^{34}\text{S}/^{32}\text{S}$  does not have the mineral specificity, rather than area specificity, thus it is characteristic for a certain geological area. That is why the sulfur isotope analysis of vermilion in wall paintings is useful to identify the origin of this pigment. However, when vermilion applied with the fresco technique it is normally mixed with gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). Gypsum, being a sulfate, might affect the sulfur isotope ratio, which can alter the isotopic results for vermilion. This study, therefore, is focused on solving this specific problem, experimentally. Gypsum, as well as vermilion, are not water-soluble. Nevertheless, gypsum is dissolved in strong acids that can be used as a method to remove only the gypsum from the mixture. We have designed an experiment to see if this was possible. Five experimental samples were prepared as it follows: 1) 100 mg of gypsum, 2) 90 mg of gypsum and 10 mg of vermilion, 3) 50 mg of gypsum and 50 mg of vermilion, 4) 10 mg of gypsum and 90 mg of vermilion, and 5) 100 mg of vermilion. Followingly, all the samples washed with either 3 ml of conc. HCl or conc.  $\text{HNO}_3$ . Insoluble part was washed with ultrapure water three times. Then, reverse aqua regia was added to the insoluble part, and the solution was heated at 95 °C for 5 hours. After cooling down, one drop of bromine was added and, the solution, again, was heated up to 95 °C for 2 hours. Subsequently,  $\text{BaCl}_2$  solution was added to the solution. The precipitated solid barium sulfate was placed into a tin cup and sulfur dioxide gas was obtained using an elemental analyzer. The sulfur dioxide was directly induced in the isotope ratio mass spectrometer. The peak height was set to about 1 nA. For the calibration, the  $^{34}\text{S}/^{32}\text{S}$  value of the Canyon Diablo meteorite was employed as a standard. The conventional ratios of  $^{34}\text{S}/^{32}\text{S}$  ( $\delta^{34}\text{S}\text{‰}$ ) were calculated. The sulfur compounds with abundant  $^{34}\text{S}$  have positive  $\delta^{34}\text{S}$  values compared to the standard, in contrary, the compounds with abundant  $^{32}\text{S}$  present negative values. The experiment led to several observations. Amongst the most important are the followings: when, either, only, the conc. HCl or only conc.  $\text{HNO}_3$  was added to all prepared samples, at room temperature, for one night, the gypsum was not dissolved. In contrary, for the sample with 10 mg of vermilion plus 90 mg of gypsum, after adding HCl and heating up to 95 °C, twice, for five hours, both gypsum and vermilion were dissolved. On the contrary, in all samples, when  $\text{HNO}_3$  was added and the same process followed, only, the gypsum was dissolved while vermilion was not. Finally, using  $\text{HNO}_3$  as dissolvent for the sample with low gypsum content (10 mg of gypsum and 90 mg of vermilion) no differences in the detected values of sulfur isotope ratio were observed compared to the values obtained for a clean vermilion specimen. In frescoes, normally, the gypsum percentage in vermilion is low (like in sample prepared with 10% gypsum + 90% vermilion). Therefore, using the procedure of washing with  $\text{HNO}_3$  and heating up to 95°C twice is suitable for analyzing isotopes in cinnabar even if we suspect that there might be some gypsum in the pigment. Consequently, the results of this study are very significant from a methodological point of view.

## Potentiometric Biosensor for Non-invasive Lactate Determination in Human Sweat

Massimo Onor<sup>1\*</sup>, Stefano Gufoni<sup>2</sup>, Tommaso Lomonaco<sup>2</sup>, Silvia Ghimentì<sup>2</sup>, Fiodor Sorrentino<sup>3</sup> and Emilia Bramanti<sup>1</sup>

<sup>1</sup> National Research Council of Italy, C.N.R., Istituto di Chimica dei Composti Organo Metallici-ICCOM- UOS Pisa, Area di Ricerca, Via G. Moruzzi 1, 56124 Pisa (Italy)

<sup>2</sup> Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 1, 56124 Pisa (Italy)

<sup>3</sup> Marwan Technology Srl, via L. Gereschi 36, 56127 Pisa, Italy

\*onor@pi.iccom.cnr.it

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**ABSTRACT:** *The present work describes a non-invasive lactate sensing in sweat during workout. The sensing system is based on a potentiometric measure performed using disposable, chemically modified, printed electrodes (sensor strips) that can be wetted with sweat during the exercise. The potentiometric signal, which is proportional to lactate concentration in sweat, is produced by a redox reaction activated by UV radiation, as opposed to the enzymatic reaction employed in traditional, blood-based measuring devices. The sensing system exhibits chemical selectivity toward lactate with linearity from 1 mM up to 180 mM. The dynamic linear range is suitable for measurement of lactate in sweat, which is more than 10 times concentrated than hematic lactate and reaches more than 100 mM in sweat during workout. The non-invasive measure can be repeated many times during exercise and during the recovery time in order to get personal information on the physiological and training status as well as on the physical performance. The device was successfully applied to several human subjects for the measurement of sweat lactate during prolonged cycling exercise. The lactate concentration changes during the exercise reflected the intensity of physical effort. During the exercise sweat was simultaneously sampled on filter paper and extracted in water, and the lactate was determined by HPLC for method comparison. This method has perspectives in many sport disciplines as well as in health care and biomedical area.*

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## New insights into understanding the optical properties of lead-based white pigments

Daniele Ciofini<sup>A</sup>, Iacopo Osticioli<sup>A\*</sup>, A.A Mencaglia<sup>A</sup>, Salvatore Siano<sup>A</sup>

<sup>A</sup>Institute of Applied Physics “Nello Carrara”.

\*i.osticioli@ifac.cnr.it

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*ABSTRACT: Lead white is the most important of lead- as well as white-pigments. It has been producing from ancient time to the present although in the nineteenth century it has lost the primacy in favor of zinc oxide (ZnO) and titanium oxide (TiO<sub>2</sub>) pigments which are less toxic and more efficient. Lead white generally refers to any lead-based white pigments however this term indicates exclusively lead carbonate hydroxide also called basic lead carbonate[(PbCO<sub>3</sub>)<sub>2</sub> Pb(OH)<sub>2</sub>]. For its high covering capacity, lead white has been used on several substrates such as on canvas and wood in paintings, on paper in manuscripts and on silk in clothes. However, it is well known that lead white could be strongly degraded when subjected to high energetic light sources causing discoloration and the formation of degradation products as massicot (PbO) and plattnerite (PbO<sub>2</sub>). This represents a limitation for the analysis of lead white by means of laser spectroscopic techniques which risk indeed damaging irreversibly the pigment. In this work a novel temperature-controlled portable-Raman device (excitation wavelength 1064 nm) has been used for lead white molecular characterization suitably modulating the output power of the laser source in order to limit undesired heating effects within the irradiated volume. This approach has allowed a systematic study of the optical properties, with particular attention to the scattering process, of different types of lead white pigments such as cerussite, hydrocerussite and anglesite which have been purchased pure on the market as well as prepared following historic recipes. Results have highlighted marked differences in optical properties according to particle dimensions and the content of impurities. X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM), Ion-Coupled Plasma (ICP) and Optical Microscopy (OM) have been also employed to characterize in depth the molecular composition of pigments as well as to define grains dimensions in order to accurately associate them to changes in the scattering process.*

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## The NOMAD (Novel Materials Discovery) Laboratory

Lorenzo Pardini<sup>A,\*</sup>, Claudia Draxl<sup>A,B</sup>, and Matthias Scheffler<sup>B</sup>[1]

<sup>A</sup>Humboldt-Universität zu Berlin, Physics Department and IRIS Adlershof, Germany — <sup>B</sup>Fritz-Haber-Institut der MPG, Berlin, Germany

\*[pardini@physik.hu-berlin.de](mailto:pardini@physik.hu-berlin.de)

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*ABSTRACT: The NOMAD (Novel Materials Discovery) Laboratory Centre of Excellence (CoE) [2], is a community-driven activity with the mission to serve the whole field of materials science and engineering. It tackles the issues of Big Data in materials science, starting from the NOMAD Repository [3], which by now contains results from more than 18 million DFT total-energy calculations from around 30 electronic-structure and force-field codes. Based on this data, we build a Materials Encyclopedia, to provide a user-friendly access to all these results, also making use of Advanced Graphics. Novel Big-Data Analytics tools are developed for finding trends, identifying outliers, and predicting new materials with tailored properties. In the near future, the project will be extended to include experimental data. This project has received funding from the European Union's Horizon 2020 research and innovation programme, grant agreement No 676580. [1] Collaboration with the whole NOMAD team [2] <https://nomad-coe.eu> [3] <https://repository.nomad-coe.eu>*

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## LIBS applied to the study of metal archaeological pieces of museum collections in Uruguay

Laura Beovide <sup>A</sup>, Moisés Knochen <sup>B</sup>, Mariela Pistón\* <sup>B</sup>

<sup>A</sup> Centro de Investigación Regional Arqueológica y Territorial, San José, DICYT-MEC, Ciudad del Plata, Uruguay; <sup>B</sup> Analytical Chemistry-DEC- Faculty of Chemistry, Universidad de la República, Avda. Gral. Flores 2124, Montevideo, Uruguay.

\*mpiston@fq.edu.uy

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**ABSTRACT:** The study of the composition of four metal objects from two archeological collections (from Europe and The Americas) now located in the Museum of Decorative Art (MDA) and the Center of Archeology (CIRAT-MEC) in Uruguay was performed for the first time since they were donated to the museum or found. This study aims to contribute to the knowledge of technological aspects related to the objects of these collections. Based on conservation criteria of metal archaeological pieces, a non-destructive technique was chosen for the diagnosis of their composition using Laser-induced Breakdown Spectroscopy (LIBS) technique. Three samples were selected from the Greco-Roman collection of the MDA, fragments of objects traditionally assigned to a classic bronze collection (2200-1800 BP). From the collection of the Center of Archeology, the only metal ornament that was recovered from the excavation VII of the Puerto La Tuna (34°42'12"; 56°24'54", Uruguay) prehispanic archaeological site was submitted to study, this ornament has a characterized chronology by <sup>14</sup>C dated in ca. 700 to 500 years BP. LIBS analyses were performed at the Institute of Chemistry of the University of Campinas (UNICAMP), Brazil, using a Quantel Brio NdYAG laser with a maximum pulse energy of 120 mJ at 1064 nm, fitted with an Andor Mechelle spectrometer with ICCD detector. The pulse energy used was 90 mJ. The strategy, in all cases, consisted of the spectral analysis from laser shots at different points on the surface of the objects, on both faces and at different depths, in the last case by series of 10 shots directed at the same point. The three samples from the presumed bronze collection showed the following results: One of them was mainly copper with presence of tin (may be compatible with the hypothesis that is bronze), however the presence of tin was low (less than 10%), in the second piece copper was the main component, no significant amounts of tin or zinc were detected (not compatible with bronze) and the third one was composed mainly by copper and tin (compatible with the hypothesis of being bronze). In this museum, these pieces had been classified as bronzes for many years and this new information contributed to better know about these collections, it can be concluded that this collection not only has pieces in bronze as it was thought, but also artifacts and ornaments made from other metals such as copper. This diagnosis using non-destructive techniques will allow to continue advancing with other archaeometric techniques in the study of the different kind of alloys present in the collection and to approach the technology used. On the other hand, the study by LIBS of the ornament found in excavation VII (La Tuna) of the Center of Archeology collection, resulted in the fact that the raw material for its manufacture was only copper. This information is very significant to the study of the prehispanic populations of Uruguay because, until now, there was no reference to the presence of this metal for prehispanic horticultural societies that occupied the Río de la Plata coast where it was found. It remains to explore the provenance of copper, whether it is from veins located in Uruguay or comes from other areas of the American continent (Andean area for example) this opens up discussing aspects of mobility and exchange of these populations in the past. Acknowledgements: Comisión Sectorial de Investigación Científica (CSIC), Agencia Nacional de Investigación e Innovación (ANII) and Prof. Celio Pasquini, UNICAMP, Brazil, for the opportunity of using the LIBS spectrometer.

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## Laser-Induced Breakdown Spectroscopy for depth-profile analysis of historical painting model samples

Eva Pospíšilová<sup>\*A</sup>, Karel Novotný<sup>A,B</sup>, Jozef Kaiser<sup>C,D</sup>, Pavel Pořízka<sup>C,D</sup>, Richard Ševčík<sup>A</sup>,  
David Hradil<sup>E,F</sup>, Janka Hradilová<sup>E</sup>

<sup>A</sup>Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, Brno, 61137, Czech Republic;

<sup>B</sup>Masaryk University, Central European Institute of Technology, Kamenice 753/5, Brno, 62500, Czech Republic;

<sup>C</sup>Brno University of Technology, Central European Institute of Technology, Purkyňova 123, Brno, 61200, Czech Republic;

<sup>D</sup>AtomTrace a.s., Kolejní 9, Brno, 61200, Czech Republic;

<sup>E</sup>Academy of Fine Arts in Prague, ALMA laboratory, U Akademie 4, Prague 7, 17022, Czech Republic;

<sup>F</sup>Institute of Inorganic Chemistry of the AS CR, v.v.i., ALMA laboratory, Husinec-Řež, 25068 Czech Republic.

\* 379264@mail.muni.cz

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**ABSTRACT:** Model multilayered painting samples containing traditional pigments were prepared on a wooden support (5 x 10 cm) with each layer partly revealed. Typical model sample consisted of three to four layers, with first, so called ground layer, containing clay or chalk in organic binder, second organic layer, and the third or in some cases fourth layer containing inorganic pigments (e.g. Azurite or Prussian Blue) in organic binder or organic dyes (e.g. Carmine Lake) with inorganic medium in organic binder. Thirty laser pulses were applied to one point and individual spectra were obtained for each shot. Broadband spectra were first acquired using Sci-Trace instrument (AtomTrace, Czech Republic) equipped with echelle spectrometer and EMCCD camera. Significant element lines were chosen and samples were re-measured using modified ablation system New Wave UP-266 MACRO equipped with Czerny Turner monochromator and an ICCD detector. Spectra obtained using both LIBS systems were processed to create the depth profiles of the samples. Particular element lines representing each layer (e.g. Cu I 324.7 nm for Azurite) were chosen. Acoustic and total emission signal was used for elimination of drift caused by the strong shot-to-shot LIBS signal variations and changes in physical-chemical properties of different layers. For comparison purposes elemental analysis by hand-held X-ray fluorescence spectrometer Innov-X DELTA Premium was used. The advantages and limitations of LIBS and hand-held XRF are discussed.

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## Characterisation of commercial alizarin-based lakes by means of spectroscopic techniques.

Pronti Lucilla<sup>\*A</sup>, Jean-baptiste Mazzitelli<sup>B</sup>, Maria Paola Bracciale<sup>C</sup>, Lorenzo Massini Rosati<sup>A</sup>, Anna Candida Felici<sup>A</sup>, Cathy Vieillescazes<sup>B</sup>, Maria Laura Santarelli<sup>C</sup>

<sup>A</sup>Dipartimento di Scienze di Base e Applicate per L'ingegneria, Sapienza-University of Rome, via Antonio Scarpa 16-00161 Rome, Italy; <sup>B</sup>Restoration engineering of Natural and Cultural Heritage – IMBE UMR 7263 CNRS – IRD 237, University of Avignon, Campus Jean-Henri Fabre - 301 rue Baruch de Spinoza - BP 2123984916 Avignon Cedex, France; <sup>C</sup>Dipartimento di Ingegneria Chimica Materiali Ambiente and CISTeC-Centro di Ricerca in Scienza e Tecnica per la Conservazione del Patrimonio Storico Architettonico, Sapienza-University of Rome, in via Eudossiana 18-00184 Rome, Italy.

\*lucilla.pronti@uniroma1.it

**ABSTRACT:** The red dyes were commonly used as artists' materials since ancient times. They are organic substances based on the anthraquinonic structure and can be achieved from insects, such as cochineal (carminic acid), kermes (kermesic acid) or can be extracted from plants, such as madder (mainly composed by alizarin). To use them in paintings, the dyes were mixed with an insoluble substrate such as aluminium hydrated, calcium carbonate or calcium sulphate; the name "lake" is referred to this latter procedure. In this work fifteen alizarin-based lakes, produced by Kremer-Pigmente and Zecchi, have been studied in order to investigate their optical and chemical features by means of Energy Dispersive X-ray Fluorescence (EDXRF), Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy (ATR-FTIR), X-ray Powder Diffraction (XRD), Liquid Chromatography coupled with a Photodiode Array (LC-PDA), UV fluorescence and reflectance spectroscopies. Almost all the lakes show alizarin as main organic compounds, one of them (23610-Kremer) presents only this anthraquinonic, indicating a synthetic dye. Lucidin primeveroside and ruberythric acid are detected in some lakes suggesting the use of "Rubia tinctorum". Most of the samples contain typical compounds present in the natural roots of madder but in two lakes (23600-Kremer and alizarin crimson-Zecchi) any anthraquinonic compounds were detected, thus they are probably synthetic dyes, as 23610 (Kremer). Furthermore several inorganic substrates, probably added during the manufacturing process, were detected. From the results obtained by UV fluorescence spectroscopy it is possible to conclude that, although it is commonly assumed that the madder lake presents an orange-pink fluorescence, the inorganic compounds induce a quenching phenomenon or an inhibition of the fluorescence.

## Total reflection X-ray fluorescence spectrometry as fast analytical technique for human placenta sample analysis.

E. Marguí<sup>\*A</sup>, P. Ricketts<sup>B</sup>, H. Fletcher<sup>C</sup>, A. G. Karydas<sup>D,E</sup>, A. Migliori<sup>D</sup>, J.J. Leani<sup>D,F</sup>, M. Hidalgo<sup>A</sup>, I. Queralt<sup>G</sup>, M. Voutchkov<sup>B</sup>

<sup>A</sup>Department of Chemistry, University of Girona, C/M. Aurèlia Campmany 69, 17003 Girona, Spain; <sup>B</sup>Department of Physics, The University of West Indies, Mona, Kingston 7, Jamaica; <sup>C</sup>Department of Obstetrics and Gynecology, The University of the West Indies, Mona, Kingston 7, Jamaica; <sup>D</sup>Nuclear Science and Instrumentation Laboratory, IAEA Laboratories, A-2444, Seibersdorf, Austria; <sup>E</sup>National Center for Scientific Research "Demokritos", Institute of Nuclear and Particle Physics "Demokritos", 15310 Aghia Paraskevi, Athens, Greece; <sup>F</sup>IFEG, National Scientific and Technical Research Council (CONICET), X5000HUA, Córdoba, Argentina; <sup>G</sup>Institute of Environmental Assessment and Water Research, IDAEA-CSIC, Jordi Girona 18-26, 08034, Barcelona, Spain

\*eva.margui@udg.edu

**ABSTRACT:** Multielement analysis of human placenta samples is of significance in many environmental and biomedical studies. In this sense, fast analytical methodologies which entail simple sample preparation and low-cost analysis are desired. In the present contribution, the possibilities and drawbacks of low-power total reflection X-ray fluorescence spectrometry (TXRF) for multielemental analysis of human placenta samples have been evaluated. The direct analysis of a solid suspension using 50 mg of powdered biological sample suspended in 1 mL of disperser agent is possible and limits of detection for most of elements are similar to those obtained using more sophisticated sample treatments such as microwave digestion (low mg/kg level). Accurate and precise results were obtained for most elements using internal standardization as quantification approach and applying a correction factor to compensate for absorption effects. The correction factor was based on the proportional ratio between the slurry preparation results and those obtained for the analysis of a set of human placenta samples analysed by microwave digestion combined with inductively coupled plasma emission spectroscopy. As a study case, the developed TXRF methodology was applied for multielemental analysis of several healthy women's placenta samples from two regions in Jamaica. Obtained results from the analysis of the target human placenta samples revealed that most minor and trace elements are homogeneously present and not significant differences were found between the studied regions. The only exceptions were Ca and Br which present a high variability between the two regions studied but also within the specimens from the same region. Additional studies are needed to find out if this variability can be related to environmental exposure of both mother and fetus.

## Decorative stones characterization through spectroscopic methods: mosaic tesserae from an outstanding late Roman *villa* in Tuscany

Raneri<sup>A\*</sup>, F. Cantini<sup>B</sup>, V. Palleschi<sup>C</sup>, S. Legnaioli<sup>C</sup>, S. Pagnotta<sup>C</sup>, G. Lorenzetti<sup>C</sup>, M. Lezzerini<sup>A</sup>

<sup>A</sup>Department of Earth Sciences, University of Pisa, Via Santa Maria, 53 – 56126 Pisa, Italy; <sup>B</sup>Dipartimento di Civiltà e forme del sapere, via dei Mille 19 - 56126 Pisa, Italy; <sup>C</sup>Applied and Laser Spectroscopy Laboratory, Institute of Chemistry of Organometallic Compounds, Research Area of National Research Council, Via G. Moruzzi, 1 – 56124 Pisa, Italy

\*simona.raneri@unipi.it

**ABSTRACT:** *In the framework of archeological investigations of an outstanding Roman villa in Tuscany (Villa dell'Oratorio, in the territory of Capraia e Limite, Florence), a characterization of decorative stones employed in mosaic tesserae have been carried out with the aim to identify the raw materials and their supply basin, and to value the ability of the villa owner and builders to obtain supplies at local or possible over local markets. The archaeological and historical context is particularly interesting. The villa, built in the middle of the 4<sup>th</sup> centuries, probably belonged to the great senator Vettius Agorius Praetextatus, remembered in an inscription found in the site. The importance of this figure in the Late Roman world is underlined by Macrobius, who defined the 4<sup>th</sup> century as the Saeculum Praetextati, and reflected by the architecture of the building with mosaics: this is a hexagonal structure, of almost 30 meters in diameter, equipped with apsed rooms (at least 5) and similar to some monumental triclinia of Constantinople, dated in the fifth century and related to the Imperial Court. The mosaics unveiled in the villa consist in cubic tesserae made by decorative stones ranging in color from white, to black, from red to yellow and green, along with blue and green glazed elements. To achieve the aim of the study, spectroscopic analysis through X-ray fluorescence (XRF), laser induced breakdown spectroscopy (LIBS) and Raman spectroscopy have been carried out, supported by classical mineralogical-petrographic methods. The obtained results have been compared with reference data on decorative stones provided in literature for ancient marbles, delineating the commercial movements undertaken the construction of Villa dell'Oratorio and supporting the archeological overview of a such relevant and unique late Roman villa in Italy.*

## Mural painting in Tuscany during the Middle Age: a spectroscopic investigation on pigments and painting technique

M. Lezzerini<sup>A</sup>, F. Cantini<sup>C</sup>, Raneri<sup>A\*</sup>, R. Belcari<sup>C</sup>, S. Pagnotta<sup>B</sup>, G. Lorenzetti<sup>B</sup>, S. Legnaioli<sup>B</sup>, V. Pallersch<sup>B</sup>

<sup>A</sup>Department of Earth Sciences, University of Pisa, Via Santa Maria, 53 – 56126 Pisa, Italy; <sup>B</sup>Applied and Laser Spectroscopy Laboratory, Institute of Chemistry of Organometallic Compounds, Research Area of National Research Council, Via G. Moruzzi, 1 – 56124 Pisa, Italy; <sup>C</sup>Dipartimento di Civiltà e forme del sapere, via dei Mille 19 - 56126 Pisa, Italy.

\*simona.raneri@unipi.it

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**ABSTRACT:** The inspection of pigmenting agents and painting techniques are some of the main archeological questions posed by artworks as wall paintings and frescoes. The identification of peculiar pigments as well as the discrimination among decorative techniques allows supporting archeological interpretations about construction phases and possible restoring actions. In the matter in fact, the possibility to acquire such information requires the application of a combined archeological and archeometric approach, supporting the historical and architectonical evidences with analytic data. That's the case of San Genesio church (San Miniato, Pisa) wall paintings, explored in the present study by spectroscopic methods, i.e.: Raman spectroscopy and portable XRF fluorescence, supported by classical minero-petrographic analysis. The studied materials consist in red, yellow, green painted fragments founded in the collapse layers of the presbytery and crypt. The church, located in the Arno valley, along the Via Francigena and the road that linked Florence to Pisa, was built in the late 7<sup>th</sup> century and enlarged between the 10<sup>th</sup> and the second half of the 12<sup>th</sup> century, when a rich village developed near the religious building. On the basis of the archeological evidences, it is possible that the wall paintings are related to the decoration of the 11<sup>th</sup>-12<sup>th</sup> century presbytery or crypt. The obtained results data have been employed to unveil raw materials and painting techniques, possible different construction phases in San Genesio church and, finally, support the archeological studies on the technological evolution of mural painting in Tuscany during the Middle Age.

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## Demonstration of eco friendly tanning cycle by spectroscopic techniques (LIFE14 ENV/IT/000443 LIFETAN)

Alice Dall'Ara<sup>\*A</sup>, Emilia Bramanti<sup>B</sup>, Mercedes Roig<sup>C</sup>, Maurizio Sabatini<sup>D</sup>, Matias Cobo<sup>E</sup>,  
Elena Salernitano<sup>A</sup>, Federica Bezzi<sup>A</sup>

<sup>A</sup> Laboratory of Materials Technologies Faenza (TEMAF), Italian National agency for new technologies, Energy and sustainable economic development (ENEA), Via Ravennana 186, 48018 Faenza (Italy); <sup>B</sup> Institute of Chemistry of Organo Metallic Compounds (ICCOM)- U.O.S. Pisa, Italian National Research Council (CNR), Via G. Moruzzi 1, 56124 Pisa; <sup>C</sup> INESCOP, Unidad Técnica Vall d'Uixó, Parc Ind. "La Vernicha", Nave 1 12600 Vall d'Uixó - Castellon, Espana; <sup>D</sup> Newport, Vc. Abruzzi 9, S. Croce sull'Arno (Pisa), Italy; <sup>E</sup> Tradelda S.L., Av San Luis de Cuba, 03600 Elda, Alicante, Spain

\*alice.dallara@enea.it

**ABSTRACT:** An eco friendly tanning cycle is proposed in the European Project Life14 ENV/IT/443 LIFETAN, with the replacement of current commercial chemical and toxic products with innovative natural products and technologies in five crucial phases: bating, defatting, tanning, dyeing and fatting. The double goal of the project is to propose: i) a chromium free tanning cycle, ii) a 20% reduction of chromium salts with the new natural products, whilst maintaining the leather high quality standards, such as the made in Italy. Each natural product was the focus of five specific previous LIFE projects (PODEBA for the bating, ECODEFATTING for the defatting, OXATAN for the tanning, BIONAD for the dyeing and ECOFATTING for the fatting phase respectively) and individually demonstrated good applicability. LIFETAN project analyses the interaction among the 5 products, involving Italian and Spanish partners. Processes/cycle with standard reagents and natural/naturalized products are compared, to check leather and leather product quality, natural product performance and environmental impact (wastewater load, wastes and LCA). Spectroscopic techniques such as SEM-EDS and ATR-FTIR Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDS), Thermogravimetric Analysis (TGA) and ATR-FTIR Spectroscopy were used to monitor the final leather quality, together with samples along the process. The introduction of natural/naturalized products did not modify leather morphology (pore size and distribution) and interaction with leather collagen. These results were accomplished with thermal behaviour and physical properties of leather. The main results of tests carried out at laboratory and semi-industrial level will be presented. (Life14 ENV/IT/443 LIFETA is co-funded by EU, within the LIFE program)



## Eco friendly leather: Energy Dispersive X-Ray Spectroscopy combined with Scanning Electron Microscopy and Thermogravimetric Analysis (LIFE14 ENV/IT/000443 LIFETAN)

Elena Salernitano<sup>\*A</sup>, Alice Dall'Ara<sup>A</sup>, Alessandra Strafella<sup>A</sup>, Emilia Bramanti<sup>B</sup>

<sup>A</sup> Laboratory of Materials Technologies Faenza (TEMAF), Italian National agency for new technologies, Energy and sustainable economic development (ENEA), Via Ravennana 186, 48018 Faenza (Italy); <sup>B</sup> Institute of Chemistry of Organo Metallic Compounds (ICCOM)- U.O.S. Pisa, Italian National Research Council (CNR), Via G. Moruzzi 1, 56124 Pisa.

\*elena.salernitano@enea.it

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**ABSTRACT:** The replacement of current commercial chemical and toxic products with innovative natural products and technologies in the whole tanning cycle (bating, defatting, fatting, dyeing and tanning phases), is the aim of the European Project Life14 ENV/IT/443 "LIFETAN: eco friendly tanning cycle". Leather production is traditionally responsible for heavy environmental impacts (hazardous substances, fatliquoring products, volatile organic compounds, etc.) and there are difficulties in recycling and disposal of semi-finished or finished products containing toxic metals, in particular chromium. The main objectives of LIFETAN project are: using natural fatliquoring and degreasing products that do not exceed the legal limits for hazardous substances in leather goods, reducing waste water contamination by enhancing the biodegradability of fatliquoring and degreasing products, recycling poultry waste to obtain technical products for the bating phase, designing natural dyes and developing an innovative chromium-free tanning technology. The compatibility of natural products for bating and defatting phase, both with Chromium and oxazolidine tanning, was demonstrated at laboratory level and the safety and ecosustainability improvement of the tanning cycle is addressed at semi-industrial level. Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDS and Thermogravimetric Analysis (TGA) were used to monitor the leather samples and to evaluate the benefits of the application of the innovative products. Different types of leather samples, subjected to partial and/or complete tanning cycle using natural products, both in a laboratory and pilot production scale-up, were analysed. The SEM-EDS was applied in order to observe the surface and cross-section morphology of leather and to provide a semi-quantitative elemental analysis, TGA to evaluate the leather thermal stability. The experimental results are also confirmed by Attenuated Total Reflectance Mid-Infrared (ATR-FTIR) Spectroscopy. (The Life 14 ENV/IT/443 LIFETAN project is co-financed by EU, within the LIFE program)

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## Development of a fitting algorithm for spectral analysis in a Laser Induced Breakdown Spectroscopy system

Roberto Sanginés<sup>\*A</sup>, Walther Lee<sup>B</sup>, Alan Preciado-Grijalva<sup>B</sup>, Oscar Hernández-Utrera<sup>A</sup>, Noemí Abundiz-Cisneros<sup>A</sup>, Roberto Machorro-Mejía<sup>C</sup>

<sup>A</sup> Cátedra Conacyt, Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Apdo. Postal 14, CP. 22800 Ensenada, B.C. México;

<sup>B</sup> Facultad de Ciencias, Universidad Autónoma de Baja California, Av. Teniente Jose Azueta, CP. 22860. Ensenada, B.C. México;

<sup>C</sup> Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Apdo. Postal 14, CP. 22800 Ensenada, B.C. México;

\*sangines@cnyun.unam.mx

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**ABSTRACT:** Laser induced breakdown spectroscopy (LIBS) has been widely used for elemental analysis of solid, liquid and gaseous samples due to its portability and the practical null sample preparation. The main drawback of this technique is the necessity of having a calibration curve to obtain quantitative information of the sample, which in some situations is virtually impossible to get. Hence, it has been developed a calibration-free algorithm<sup>1</sup> which provides the composition of the sample by assuming a Boltzmann distribution of all species within the ablation plasma, where spectroscopic information of all of them is required. In this work a semi-automatic algorithm to identify and deconvolute emission peaks of the plasma spectrum is presented, as well as its lorentzian function fitting. The code also relates each emission peak found in the ablation plasma to those listed in the NIST atomic spectra database, so the qualitative composition of the sample is granted. We have explored the limit of detection of a miniature spectrometer to develop an inexpensive portable system and eventually, along the fitting parameters as well as considerations on Local Thermal Equilibrium and an optically thin plasma, to implement it in a calibration-free procedure in the future. 1. Tognoni, E. et al., "Calibration-Free Laser-Induced Breakdown Spectroscopy: State of the art", *Spectrochimica Acta, Part B* 65 (2010) 1-14

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## Direct determination of $\text{TiO}_2$ as Ti used as digestibility marker in bovine faeces by Laser-Induced Breakdown Spectroscopy (LIBS)

Ana Beatriz Santos da Silva<sup>\*A,B</sup>, Edenir Rodrigues Pereira-Filho<sup>A</sup>, Ana Rita de Araujo Nogueira<sup>B</sup>

<sup>A</sup>Grupo de Análise Instrumental Aplicada, Departamento de Química, Universidade Federal de São Carlos, 13565-605, São Carlos, São Paulo, Brazil <sup>B</sup>Embrapa Pecuária Sudeste, 13560-970, São Carlos, São Paulo, Brazil.

\*ana.beatriz30@hotmail.com

**ABSTRACT:** Digestibility in animals is measured by indirect methods that consist in the use of markers, which are inert substances not absorbed or metabolized along the digestive tract. Titanium dioxide ( $\text{TiO}_2$ ) has attractive properties as digestibility marker: is not toxic, inert and has physical and chemical stability<sup>1</sup>. The goal of this study was to develop a method to directly quantify  $\text{TiO}_2$  as Ti, used as digestibility marker in bovine faeces by laser-induced breakdown spectroscopy (LIBS)<sup>2</sup>. A bovine faece was directly collected from the rectum of the animals. Afterward, it was dried in an oven at 65 °C for 48 hours and milled in a knife mill of stainless steel with a sieve of 1 mm. This sample was divided into several aliquots that were weighted and pressed by a hydraulic press to the form of a pastille (around 10 mmØ). LIBS operating parameters energy, delay time, and spot size were optimized, and full experimental design ( $2^3$ , 8 experiments) were performed. Then the energy was kept constant at 80 mJ, and a central composite design was applied (11 additional experiments). In both cases, the responses monitored were signal/background ratio (SBR) of three Ti emission lines (334.2; 334.9 and 368.5 nm). Regarding the calibration of this technique, analyte-free aliquots were employed, Ti as  $\text{TiO}_2$  was added in increasing amounts ( $\text{TiO}_2$  from 0 to 1.2 %  $\text{m m}^{-1}$ ), and the accuracy was evaluated using three aliquots with known  $\text{TiO}_2$  concentrations. In each analysis, approximately 400 spectra per sample were obtained, and the raw data was treated with 12 types of normalization/standardization<sup>3</sup>. Later, signals area and height were calculated for each emission line mentioned above. In the optimization, was observed that delay time and spot size are the most important variables and they have a positive effect. For the analysis, the best conditions were 100  $\mu\text{m}$  for spot size, 0.6  $\mu\text{s}$  for delay time and 80 mJ for energy. Concerning the calibration, standard error of calibration (SEC), and coefficient of determination ( $R^2$ ) were calculated. Low values of SEC were determined in emission line 334.9 nm: 0.16% for the area and 0.15% for the height. The coefficient of determination value in this line is close of 1. The average of the area normalized by the norm shows the best results because was the treatment with the highest sensitivity, linearity ( $R^2 = 0.96$ ), and the linear model of calibration has 88% of predictably. About the accuracy, the three aliquots were quantified, and the highest relative error when predicted and reference values were compared was 30%. The calculated standard error of prediction (SEP) was 0.13%. The limit of detection (LOD), assessed according to the recommendation of IUPAC, was 0.06 % ( $\text{m m}^{-1}$ ). Therefore, LIBS is an alternative because it has an adequate sensitivity for this type of analysis, and the main advantage is the direct determination of  $\text{TiO}_2$  which is a difficult decomposition substance. The authors are grateful to Conselho Nacional de Desenvolvimento Tecnológico e Científico (162318/2014-6; 307639/2014-2), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), and Fundação de Amparo à Pesquisa do Estado de São Paulo (2012/01769-3 and 2015/14488-0). <sup>1</sup>Titgemeyer EC1, Armendariz CK, Bindel DJ, Greenwood RH, Löest CA., J Anim Sci. 2001 Apr;79(4):1059-63. <sup>2</sup>Pasquini, C.; Cortez, J.; Silva, L. M. C.; Gonzaga, F. B., J. Braz. Chem. Soc., 18(3), 463, 2007. <sup>3</sup>Castro, J.; Pereira-Filho, E. R., J. Anal. At. Spectrom., 31,1949, 2016.

## Iron, Copper and Zinc mapping analysis of Swiss mice brains on experimental model of Alzheimer's disease induced by $\beta$ -amyloid oligomers

Danielle Santos de Almeida<sup>A\*</sup>, Matheus de Melo Brígido<sup>B</sup>, Marcelino José dos Anjos<sup>B</sup>, Sergio Teixeira Ferreira<sup>C,D</sup>, Amanda Santos de Souza<sup>C,D</sup>, Ricardo Tadeu Lopes<sup>A</sup>

<sup>A</sup>Nuclear Instrumentation Laboratory, Federal University of Rio de Janeiro, <sup>B</sup>Physics Institute - State University of Rio de Janeiro, <sup>C</sup>Institute of Biophysics Carlos Chagas Filho - Federal University of Rio de Janeiro, <sup>D</sup>Institute of Medical Biochemistry Leopoldo de Meis - Federal University of Rio de Janeiro.

\*dani.almeida84@gmail.com

**ABSTRACT:** Alzheimer's disease (AD) is a progressive dementia that, in early stages, manifests as a profound inability to form new memories. Its incidence is higher in people aged over sixty-five years. The basis for this specificity is unknown, but some evidences point to the involvement of neurotoxins derived from the self-associating  $\beta$ -amyloid ( $A\beta$ ).  $A\beta$  generates the fibrils of the hallmark amyloid plaques of AD. However, the "fibril hypothesis" fails to explain crucial clinical and pathological aspects of several degenerative diseases. In AD, it has been pointed out that there is poor or even the absence of correlation between plaque burden and dementia. Soluble oligomers are found at elevated levels and in association with synapses in the brains of demented AD individuals. The buildup of  $\beta$ -amyloid oligomers ( $A\beta$ os) in the affected brains has been recognized as an additional neuropathological hallmark of AD. Interestingly, several groups have raised the "metal hypothesis" of AD. Several metal ions, such as zinc, iron, and copper are all increased in the aged brain. There is evidence that the modification of homeostasis of metal ions leads to neuronal death. Redox metal ions are instrumental in enhancing the production of reactive oxygen species (ROS), contributing to oxidative stress and inflammation of the brain of Alzheimer's patients. Metal ions, such as copper and zinc, have been demonstrated to modulate amyloid aggregation along different pathways. In the brain of patients with AD, the Fe accumulation contributes to  $A\beta$  aberrant aggregation and toxicity. So, the metal ions may have an important impact on the protein misfolding and the progression of the neurodegenerative process. The development of the synchrotron radiation microbeam X-ray fluorescence technique ( $\mu$ SRXRF) provided new opportunities for biomedical applications. The  $\mu$ SRXRF technique, in this analysis, is very important, because the construction of two-dimensional maps of mice brains with AD is fundamental to understanding this disease, and the application of neuroprotective and therapeutic approaches. The levels of trace elements are distributed heterogeneously in the brain. For the essential elements, the concentration is probably related to the physiological functions of specific brain areas. Deviations of normal trace element levels have been correlated with AD. With the use of TXRF technique, it was verified that the elementary homeostasis in mice brains (on experimental model of AD induced by  $A\beta$ os) changed. Besides that, in mice brains, these elements concentrations occur in the order of  $\mu\text{g.g}^{-1}$ . The purpose of this study is to evaluate the Fe, Cu, and Zn spatial distribution (2D) in brain regions impaired by AD, using the  $\mu$ XRF technique. In this study, AD is induced by a single intracerebroventricular injection of  $A\beta$ os.  $A\beta$ os are linked to neuronal dysfunction in brain areas related to learning and memory, such as hippocampus, and they have an impact on the hypothalamus, which plays essential functions in the central and peripheral nervous system. Thus, it is possible that, in the AD brain, progressive accumulation of  $A\beta$ os brings about different functional outcomes in brain regions responsible for metal spatial distribution.  $A\beta$ O-induced inflammation in the hippocampus and hypothalamus may be especially relevant in terms of disrupting hypothalamic insulin, signaling that it is involved in the damage found in the AD. Possible differences in the elemental concentration findings for some regions of the brain with AD, in the present work, suggest an association between disruption of homeostasis in the metal spatial distribution and AD.

## A multi-technique approach for determining the provenance of the mineral fluorite used as an artistic pigment

Radka Šefců<sup>\*A</sup>, Jiří Mizera<sup>B</sup>, David Koloušek<sup>C</sup>

<sup>A</sup> National Gallery in Prague, Staroměstské nám. 12, 110 15 Prague, Czech Republic; <sup>B</sup> Nuclear Physics Institute of the CAS, v. v. i. Řež 130, 250 68 Řež, Czech Republic; <sup>C</sup> University of Chemistry and Technology Prague, Technická 5, 166 28 Prague, Czech Republic

\*radka.sefcu@ngprague.cz

Fluorite (also known as Fluorspar) is a mineral with variable color a member of the Halide family with chemical composition  $\text{CaF}_2$ . His dark purple variety called antozonite was used as a very specific pigment on Bohemian panel paintings and polychromed sculptures in a relatively short period of time in the Late Gothic and Early Renaissance period, approximately from 1480 to the half of the 16<sup>th</sup> century. The survey in the chemical-technological laboratory of the National Gallery in Prague proved use of purple fluorite on the paintings from several regions of Bohemia, especially Northern, Eastern, Central Bohemia and Silesia. But it was also authenticated on the artworks from Poland, Germany and Austria. Unfortunately, the natural sources of the fluorite (antozonite) as an artistic pigment have not been clearly identified yet. Fluorite usually occurs together with deposits of silver, copper, lead, zinc or also limestone and dolomite. The mineralogical characteristics of fluorite vary according to the source. Dark purple to black color is typical for fluorite deposits containing also radioactive elements. It was shown that the presence of various rare earth elements also has an effect on the fluorite color. Important deposits in the Central Europe are especially in Germany. The most probable sources of fluorite as a pigment are in Nabburg-Wölsendorf in the Southeast Germany where the specific variety antozonite occurs. Purple fluorite also occurs in the Czech Republic – earlier it was localized in the mines in Joachimsthal (Jáchymov). For a long time, there has been an interest in determining the provenance of the mineral for the pigment preparation. Comparative analysis of the fluorites in the paintings and the natural minerals from various European locations may provide such information. In 2013 systematic characterization of purple fluorites of known provenance – Nabburg and Wölsendorf in Germany, Castleton and Derbyshire in England, fluorite from Bohemia (Joachimsthal, Cinvald, Krupka and Slavkov) started in order to create a database for the provenance recognition. The main results of the analyses are summarized in this work. A multi-technique approach was adopted to find chemical markers for discriminating different fluorite sources. Panting micro-samples were investigated by standard methods: optical microscopy (OM) and elemental analysis via scanning electron microscopy with X-ray microanalysis (SEM/EDS). The most significant results were obtained by micro-Raman spectroscopy (MRS) and neutron activation analysis (NAA). Both methods together with X-ray fluorescence (XRF) were used for analyses of the samples of natural minerals. MRS showed the characteristic bands and XRF specified the major elemental composition of each sample. NAA allowed assaying fluorine and numerous major and trace elements. Obtained results showed considerable variation in the composition of the natural mineral fluorite. The interpretation of the results measured on samples of paint layers was complicated due to the predominant content of other pigments, and in NAA also due to interference from fission of uranium present in samples. On the other hand, high uranium and low thorium contents in painting samples may point to Nabburg-Wölsendorf as probable source deposits of violet fluorite. Collected data enables further comparative analysis and characterization of the potential sources of fluorite for the preparation of the artistic pigment.

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## The characterization of materials from the Norbert Grund's paintings on metal plate support

Radka Šefců\*<sup>A</sup>, Marcela Vondráčková<sup>A</sup>, Tomáš Trojek<sup>B</sup>, Václav Pitthard<sup>C</sup>

<sup>A</sup> National Gallery in Prague, Staroměstské nám. 12, 110 15 Prague, Czech Republic; <sup>B</sup> Czech Technical University in Prague, Department of Dosimetry and Application of Ionizing Radiation, Břehová 7, 115 19 Prague, Czech Republic; <sup>C</sup> Kunsthistorisches Museum, Burgring 5, 1010 Vienna, Austria

\*radka.sefcu@ngprague.cz

*The present paper reveals a characterization of painting materials from Norbert Grund's paintings on the metal plate support that came into being during 1750s and 1760s. Norbert Grund (1717–1767) is one of the most important representatives of Rococo painting in Bohemia. Great popularity of his paintings is documented by inventory records and the numerous works produced by imitators, copyists and followers. The research concerning Grund's painting technique enabled, among others, to distinguish the original author's works and paintings by imitators and followers. In the collection of the National Gallery in Prague there are more than 40 paintings on metal support by Norbert Grund. The small-size cabinet paintings on metallic supports represent a considerable part of his oeuvre. The metal materials could provide a rigid and smooth surface to paint, however, their size was a partial limitation. The size of small-format paintings is typically not bigger than 30 by 40 cm, but usually their dimensions do not exceed 15 to 25 cm. The painting technique on metal plate required special methods of the preparation of the support and materials used. To identify the painting technique and materials, non-invasive and non-destructive analytical techniques were used, such as X-ray fluorescence (XRF), Optical Microscopy (OM), Scanning Electron Microscopy coupled with Energy Dispersive X-Ray Spectroscopy (SEM-EDS) were used. The most significant results were obtained by micro-Raman spectroscopy (MRS). Analyses were performed on the individual pigment grains or on the cross sections using the mapping mode for the identification of individual components present in the colour layers. MRS analyses were performed with Raman microscope Nicolet DXR (Thermo Scientific, USA) in combination with an Olympus confocal microscope. Each spectra were recorded in the 3000 to 50 cm<sup>-1</sup> spectral range. The spectral resolution was 4 cm<sup>-1</sup>. Two lasers were used as the excitation source with wavelength of 532 nm (diode laser) and 780 nm (diode laser). Spectral data were elaborated with Omnic 9.2 (Thermo Nicolet Corporation) software. Furthermore, chromatography - mass spectrometry (GC-MS) technique was applied to specify the presence of lipid and resinous binding media. The emphasis was stressed on the handling of the ground and paint layers. Thanks to the analytical methods, it was possible to determine the exact materials used for supports, as well as the composition of pigments and binding media in different layers. The most numerous group includes supports made of iron plates coated with tin layer. though copper and brass supports were also identified. In addition, the surface corrosion products of metallic materials were documented. A palette of white, yellow, red, blue and black pigments was identified. The individual pigments as lead white, vermilion, earth pigments, lapis lazuli, carbon-based blacks and the most important pigment Prussian blue were detected. Walnut oil or linseed oil with additions of softwood resins were determined as major binding media of paint layers. The research of materials opened, among other things, a discussion about the authorship of some works previously attributed to Norbert Grund. The identification of blue pigment by micro-Raman spectroscopy has proved its importance. The dominant use of Prussian blue seems to exclude the use of other blue pigments in paintings by Grund. The results of this research allowed us to evaluate the materials of his palette and specify the painting techniques on the metal support in the 18<sup>th</sup> century. The work was realized thanks to the means of the project Norbert Grund (1717-1767) of the program Czech Science Foundation, GACR, Identification code: GA13-07247S.*

## Comparative analysis of casting technologies used for the manufacturing of cast iron dishware in the towns of Volga Bulgaria in 13th-15th centuries (Tatarstan, Russia)

Eugenia Shaykhutdinova<sup>\*A-C</sup>, Rezida Khramchenkova<sup>A,B</sup>, Alexander Belyaev<sup>A</sup>, Airat Sitdikov<sup>A,B</sup>, Ruslan Yanbaev<sup>C</sup>

<sup>A</sup> Restoration & Analytical Department, Archaeology Institute named after A. Kh. Khalikov of the Tatarstan Academy of Sciences, Kazan, Russian Federation; <sup>B</sup> Kazan Federal University, Kazan, Russian Federation; <sup>C</sup> Department of Technology of Machinery Production, Kazan National Research Technical University named after A.N.Tupolev - KAI, Kazan, Russian Federation.

\* eugen.shaykhutdinova@gmail.com

**ABSTRACT:** The availability of a ferrous metallurgy craft school in the territory of Volga Bulgaria in the period of 13th-15th centuries is confirmed by archaeological findings. However, a wide variety of cast iron articles and the instability of trade and craft centres in 13th-15th cc. brings up the issue of the continuity of cast iron technologies used in the leading towns of Volga Bulgaria, and the possible import of articles from other centres of the Golden Horde. One of the most significant industries of Volga Bulgaria (Republic of Tatarstan, Russian Federation) was ferrous metallurgy. The existence of Bolgar cast iron manufacturing in the Golden Horde period (13th-15th cc.) is indicated by numerous archaeological fragments of cast iron cauldrons and the remains of large kilns. The work features a comparative analysis of the research of cast iron dishware items dating back to the period of Volga Bulgaria's decline and the emergence of a new regional trade and craft centre - the town of Kazan. Artefacts from excavations in Bolgar, Juketau and Kazan were studied using the techniques of scanning electron microscopy and emission spectral analysis. All studied items have the composition of steel-making iron. Their random or laminar highly dispersed structure signifies that the technology of cast iron production was imperfect. The structure consists of complex phases which can be generally classified into grains of white cast iron with graphite, grey cast iron with graphite, and a boundary layer featuring a complex irregular microelemental composition. Items from Kazan are characterized by a wide diversity in terms of structure and chemical composition. Their structure is distinguished by a clearer separation of dendritic phases with a complex multiphase structure. The micro-trace analysis of their composition revealed an unusual peculiarity which resides in the fact that Bolgar and Juketau cast iron contains aluminium, silicon and manganese, whereas the cast iron from Kazan is characterized by a greater diversity in terms of trace impurities. Practically all items contain a large amount of phosphorus, which indicates that wood was used as fuel in the production of cast iron. The cast iron industry of Volga Bulgaria in the late 13th - early 15th centuries was at an early stage of development and presumably developed independently from the other states of the Golden Horde. Cast iron dishware discovered in Kazan is characterized by its great diversity. This can be due to different craft schools, as well as the fact that the articles could have been imported from other regions of the Golden Horde.



## Comparative investigation of toxicity; bioaccumulation and distribution of Cd-based Quantum dots and Cd salt in freshwater plant *Lemna minor*

Pavlna Škarková<sup>1</sup>, Karel Novotný<sup>2,3</sup>, Pavel Pořízka<sup>1,3</sup>, Jakub Klus<sup>1,3</sup>,  
Přemysl Lubal<sup>2</sup>, Jozef Kaiser<sup>1,3</sup>

<sup>1</sup>Central European Institute of Technology (CEITEC) Brno University of Technology, Technická 3058/10,  
616 00 Brno, Czech Republic

<sup>2</sup>Central European Institute of Technology (CEITEC) Masaryk University, Kamenice 5, 625 00 Brno, Czech  
Republic

<sup>3</sup>AtomTrace, Kolejní 9, 612 00 Brno, Czech Republic

Pavlna.Skarkova@ceitec.vutbr.cz

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**ABSTRACT:** Quantum dots (QDs) are fluorescent semiconductor nanocrystals with increasing use, mainly as labels for tagging or imaging in biological systems<sup>1</sup>. Like other classes of nanomaterials, they may eventually find their way into the environment. Thus it is of a high importance to research the toxicity of Cd-based QDs to environmental organisms, which may come into contact with QD-containing products when they are discarded. The purpose of this study was to determine the toxicity of two different sources of cadmium, i. e. CdCl<sub>2</sub> and Cd-based QDs, for freshwater model plant *Lemna minor*. Cadmium telluride QDs were capped with two coating ligands: glutathione (GSH) or 3-mercaptopropionic acid (MPA). Growth rate inhibition and final biomass inhibition of *L. minor* after 168-hour exposure were monitored as toxicity endpoints. Dose-response curves for Cd toxicity and EC50<sub>168h</sub> values were statistically evaluated for all sources of Cd to uncover possible differences among the toxicities of tested compounds. We also determined the total content of Cd and its bioaccumulation factors (BAFs) in *L. minor* after the exposure period to distinguish Cd bioaccumulation patterns with respect to different test compounds. Laser-Induced Breakdown Spectroscopy (LIBS) with lateral resolution of 200 µm was employed in order to obtain two-dimensional maps of Cd spatial distribution in *L. minor* fronds. Our results show that GSH- and MPA-capped Cd-based QDs have similar toxicity for *L. minor*, but are significantly less toxic than CdCl<sub>2</sub>. However, both sources of Cd lead to similar patterns of Cd bioaccumulation and distribution in *L. minor* fronds. Our results are in line with previous reports that the main mediators of Cd toxicity and bioaccumulation in aquatic plants are Cd<sup>2+</sup> ions dissolved from Cd-based QDs. Financial support from the project CEITEC 2020 (LQ1601) from European Regional Development Fund is highly acknowledged. References: <sup>1</sup>Jamieson, T., Bakhshi, R., Petrova, D., Pocock, R., Imani, M., Seifalian, A.M. Biological applications of quantum dots. *Biomaterials* 2007; 28: 4717–4732. doi:10.1016/j.biomaterials.2007.07.014

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## Non-invasive spectroscopic study on a modern reverse glass painting: Marianne Uhlenhuth's "Ohne Titel, 1954"

Simon Steger<sup>\*A</sup>, Oliver Hahn<sup>AB</sup>, Ira Rabin<sup>AB</sup>, Heike Stege<sup>C</sup>

<sup>A</sup>Department of Materials and the Environment, Federal Institute for Materials Research and Testing (BAM), Berlin, Germany; <sup>B</sup>Centre for the Study of Manuscript Cultures, University of Hamburg, Hamburg, Germany; <sup>C</sup>Döerner Institut, Bayerische Staatsgemäldesammlungen, München, Germany

\*simon.steger@bam.de

*We present a spectroscopic study of the reverse glass painting "Ohne Titel" created by Marianne Uhlenhuth in 1954. In contrast to stained glass technique, reverse glass painting doesn't involve a firing step. Popular in the Renaissance it was nearly forgotten in the 18th century to be rediscovered in the beginning of the 20th. In this time, invention of new inorganic and synthesis of new organic pigments in combination with supersession of traditional colorants resulted in experimental works and sometimes remarkable pigment mixtures. The abstract painting under study was executed in a broad palette of colorants ranging from traditional to experimental. Using a multi instrumental and non-invasive approach we investigated pigments and binding media. We carried out in-situ measurements using Raman spectroscopy (i-Raman®Plus, Bwtek inc., 785 nm, 20× objective, resolution 4 cm<sup>-1</sup>), X-ray fluorescence (Tracer III-SD, Bruker AXS Microanalysis GmbH, 40 kV, 15 μA), VIS spectroscopy (SPM 100, Gretag-Imaging AG) and DRIFTS: Diffuse Reflection-Infrared-Fourier-Transform Spectroscopy (ExoScan, Agilent GmbH, 4000 – 650 cm<sup>-1</sup>, 256 scans, spectral resolution 4 cm<sup>-1</sup>). Phthalocyanin green (PG7, Colour Index No. 74260), viridian and emerald green (copper(II) acetate triarsenite) were used for the green areas. The yellow parts consist of chrome yellow and cadmium yellow. Hansa yellow G (PY1, C.I. 11680) was used for the dark yellow/orange part. Red areas were characterized by the presence of cadmium and selenium (cadmium red) in the XRF spectrum. Ultramarine was detected in the blue parts. Concerning the violet color PR81 (bluish red, Rhodamine 6G, C.I. 45160:1) in mixture with PG7 (bluish green, C.I. 74160) were identified as main components. We want to outline that PR81 was rarely found in paintings. PR81 was only recorded in the palettes of Lucio Fontana [1,2] and Mary Cassatt [3]. The dark violet areas consist of Prussian blue and an unknown red (organic) colorant. Brown iron oxide was identified as the brown pigment. Bone black in mixture with black iron oxide were used as black materials and zinc white and titanium white as white pigments. XRF analysis of the metal color yields intense copper, zinc and nickel peaks (intensity ratio 3:3:1), which corresponds to "new silver" alloy. Barite and chalk appear as fillers in this painting. Results of DRIFTS spectra show gum sometimes mixed with protein or oil (metal soaps) as binding media. The results point out that reverse glass paintings from the classic modern period are excellent examples to study the evolution of new pigments and their acceptance in artist's palettes. [1] P. Gottschaller, N. Khandekar, L.F. Lee, D.P. Kirby, The evolution of Lucio Fontana's painting materials, Stud. Conserv. 57(2012) 76–91 [2] C. Zaffino, A. Passaretti, G. Poldi, M. Fratelli, A. Tibiletti, R. Bestetti, I. Saccani, V. Guglielmi, S. Bruni, A multi-technique approach to the chemical characterization of colored inks in contemporary art: The materials of Lucio Fontana, J. Cult. Herit. (2016), <http://dx.doi.org/10.1016/j.culher.2016.09.006> [3] C.L. Brosseau, K.S. Rayner, F. Casadio, C.M. Grzywacz, R.P. Van Duyne, Surface-Enhanced Raman Spectroscopy: A Direct Method to Identify Colorants in Various Artist Media, Anal. Chem. 81(2009) 7443–7447*

## X-ray fluorescence microanalysis of cucumber hypocotyls using synchrotron radiation

I. Szalóki\*, G. Radócz, A. Gerényi

Institute of Nuclear Techniques, Budapest University of Technology and Economics,  
Műegyetem rkp. 9, 1111 Budapest, Hungary

\*szaloki@reak.bme.hu

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**ABSTRACT:** Significant portion of plants accumulate toxic elements and transport them from roots to the leaves. The compounds of the toxic elements should strongly influence the metabolic processes; however, some plants are able to defend against this phytotoxicity by biochemical mechanism. For example, the oxidation state of elements in the nutrient should change after the uptake caused by metabolic processes [1]. In order to study the ion-transport mechanisms the distribution of chemical elements in hypocotyl of cucumber as a model organism were investigated. Cryogenic XRF micro-tomography and confocal imaging at HASYLAB Beamline L were applied for quantitative determination of distributions of toxic elements in hypocotyls. The lateral resolution of excitation synchrotron beam was 20 $\mu$ m with energy of 12.5, 17 and 22 keV providing optimal excitation condition. As a result of these experiments, elementary maps of interested elements such as Cr, Mn, Ni, Zn, Cu and As were measured and calculated in optional cross-sections of hypocotyls samples. In micro tomography measuring mode the plant samples were excited in its original biological state with cooling by liquid nitrogen stream in order to limit the beam damage effect in the sample tissue should cause by the high flux of synchrotron beam. For neglecting the beam damage effect another experimental solution was applied with combination of confocal measuring setup and the application of lyophilised cucumber samples. In order to improve the sensitivity of the 2D analysis we have developed the optimal measuring conditions for the experiments: fit the excitations energy to the atomic number of the elements, setting the optimal sampling frequency in the continuous measurement, selection of the accusation time etc. By setting the size of the voxels an improved lateral resolution of the elementary maps was achieved. Applications of these optimal measuring conditions single biological cells on the elementary maps of the hypocotyls were visible. A new quantitative algebraic reconstruction model [2] for evaluation of confocal micro X-ray fluorescence data has been developed for light matrixes (i. e. biological samples) and it was applied for determination of the elementary distributions. This theoretical model uses a generalized FPM approach to calculate 2D distribution of the concentration of the detected elements. In order to solve the non-linear system of equations describing the FPM calculation a new type of iterative algorithm was developed in MATLAB programing environment for 2D confocal imaging using monoenergetic synchrotron radiation for excitation of the sample.

**ACKNOWLEDGEMENTS:** This work has been partly carried out in the frame of VKSZ-14-1-2015-0021 Hungarian project supported by the National Research, Development and Innovation Found. The synchrotron radiation measurements were carried out at the light source DORIS III at DESY. [1] A. Gerényi, V. Czech, F. Fodor, L. Vincze, I. Szalóki, In-vivo XANES measuring techniques for studying the arsenic uptake in cucumber plants, X-Ray Spectrometry, 2016, DOI 10.1002/xrs.2730. [2] I. Szalóki, A. Gerényi, G. Radócz, A. Lovas, B. De Samber and L. Vincze, FPM model calculation for micro X-ray fluorescence confocal imaging using synchrotron radiation, Journal of Analytical Atomic Spectrometry, 2017, 32, 334–344, DOI: 10.1039/c6ja00161k.

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## Characterization of fibrotic liver tissue by LIBS

Estrella Teran-Hinojosa\*, Hugo Sobral,

Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México, Mexico City, Mexico.

\*momo@ciencias.unam.mx

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**ABSTRACT:** *Laser-Induced Breakdown Spectroscopy (LIBS) is an optical technique that allows fast multi-elemental analysis of different types of samples. In the last years, LIBS has been developed for various applications including biological samples due to its ability to distinguish among different bacterial strains [1], normal and malignant tumor cells [2] and others. In this work, rat liver tissues with different stages of fibrosis were characterized by LIBS. Liver fibrosis was induced in Wistar rats by injecting carbon tetrachloride (CCl<sub>4</sub>) and evaluated by using the Metavir scoring system. Previous to the analysis, samples were desiccated in a vacuum chamber at 10<sup>-3</sup> Torr. LIBS measurements were carried out by using a Nd:YAG laser (operated at 1064 nm, 1 Hz repetition rate and 50 mJ per pulse) to ablate the sample. Light was collected using an optical-fiber bundle and analyzed with an echelle spectrometer attached to an ICCD camera in the spectral range 200-820 nm. Depth profiling in different sample positions was performed and line transitions belonging to Mg, Ca, Na, K, Fe and P were investigated. It was observed that as the laser penetrated into the sample, the emission intensity showed large fluctuation between consecutive shot; this is due to variations of electron density and temperature of the laser produced plasma. In order to decrease the relative standard deviation (RSD) between successive shot intensities, a correction was implemented [3]. This procedure reduced the signal fluctuations (RSD) in a factor of about 2. LIBS signal shows that liver tissues with the highest level of fibrosis exhibit an increment of calcium in a factor of 3 compared with a healthy liver tissue. Other elements such as carbon and potassium did not present significant changes. [1] M. Baudelet, J. Yu, M. Bossu, J. Jovelet, J.P. Wolf, *Applied Physics Letters* 89, 163903 (2006), pp. 1–3. [2] A. Kumar, F.Y. Yueh, J.P. Singh, S. Burgess, *Applied Optics*, 43 (2004), pp. 5399–5403. [3] V. Lazic, A. Trujillo-Vazquez, H. Sobral, C. Márquez, A. Palucci, M. Ciaffi, M. Pistilli, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 122 (2016), pp. 103-113.*

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## The elemental concentration of blood serum of patients with autoimmune diseases determined by MP-AES method

Csilla Noémi Tóth<sup>\*A</sup>, Edina Baranyai<sup>A</sup>, István Csípő<sup>B</sup>, Tünde Tarr<sup>B</sup>, Margit Zeher<sup>B</sup>,  
József Posta<sup>C</sup>, István Fábán<sup>C</sup>

<sup>A</sup>Agilent Atomic Spectroscopy Partner Laboratory, Department of Inorganic and Analytical Chemistry,  
University of Debrecen, Egyetem square 1. H-4032, Debrecen, Hungary

<sup>B</sup>Division of Clinical Immunology, Medical Faculty, University of Debrecen, Moricz Zs. str. 22. H-4032,  
Debrecen, Hungary

<sup>C</sup>Department of Inorganic and Analytical Chemistry, University of Debrecen, Egyetem square 1. H-4032,  
Debrecen, Hungary

\*toth.csilla.noemi@science.unideb.hu

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**ABSTRACT:** Systemic lupus erythematosus (SLE) and Sjögren's syndrome (SS) are systemic autoimmune diseases with complex symptoms and pathogenesis that are still not completely understood. Several studies showed that the trace element homeostasis is changed in autoimmune disorders, however the results are controversial. In this study the potassium (K), calcium (Ca), magnesium (Mg), copper (Cu), zinc (Zn) and iron (Fe) concentration of the serum of patients with SLE and SS was determined by microwave plasma atomic emission spectrometry. The MP-AES 4100 (Agilent Technologies) instrument was launched to the market in 2011 which excitation source is supplied by nitrogen gas resulting in the most cost-effective method in today's atomic spectrometry. According to our results the Ca and K levels were found to be decreased in the case of both SLE and SS disorders compared to the control group and the competitive antagonism of Cu and Zn was also observed: elevated Cu concentration together with a lower Zn concentration was measured in the sera of patients with autoimmune diseases. Acknowledgement: Csilla Noémi Tóth was supported by the European Union and the State of Hungary, co-financed by the European Social Fund in the framework of TÁMOP 4.2.4. A/2-11-1-2012-0001 'National Excellence Program'. The research was supported by the EU and co-financed by the European Regional Development Fund under the project GINOP-2.3.2-15-2016-00008. We would like to highly acknowledge Agilent Technologies (Novo-Lab Ltd.) for providing the MP-AES 4200 instrument for the elemental analysis.

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## FTIR and Raman Spectroscopic Studies of Selenium Nanoparticles Synthesised by the bacterium *Azospirillum thiophilum*

A.V. Tugarova\*, P.V. Mamchenkova, Yu.A. Dyatlova, A.A. Kamnev

Laboratory of Biochemistry, Institute of Biochemistry and Physiology of Plants and Microorganisms, Russian Academy of Sciences, 13 Prosp. Entuziastov, 410049, Saratov, Russia

\*tugarova\_anna@mail.ru

**ABSTRACT:** The genus *Azospirillum* includes more than 15 species of bacteria which occupy different ecological niches. It has been shown [1] that *A. brasilense* (strains Sp245 and Sp7), a ubiquitous and most widely studied phytostimulating rhizobacterium of the genus *Azospirillum*, can reduce selenite ( $\text{SeO}_3^{2-}$ ) to elementary selenium ( $\text{Se}^0$ ) in the form of Se nanoparticles (Se NPs; nanospheres, 50–400 nm in size). Using strain *A. brasilense* Sp7, a scheme has recently been developed for the synthesis of extracellular Se NPs more homogeneous in size (around 90 nm in diameter); their zeta potentials were determined, and the Se NPs obtained were characterised by FTIR spectroscopy [2]. In this work, extracellular Se NPs were synthesised for the first time by *Azospirillum thiophilum* (strain VKM B-2513) using the same scheme [2] in the presence of 5 mM  $\text{Na}_2\text{SeO}_3$  and comparatively studied. *A. thiophilum* is a recently described species isolated from a sulphur bacterial mat collected from a sulphide spring [3]. The Se NPs obtained were separated including the removal of bacterial cells by centrifugation and filtration, purified by triple washing in saline solution, and concentrated. The resulting Se NPs were characterised by FTIR spectroscopy (as a dried layer on a ZnSe disc in the transmission mode) and Raman spectroscopy. For Se NPs produced by both *A. brasilense* Sp7 and *A. thiophilum*, Raman spectra in the low-frequency region (under  $500\text{ cm}^{-1}$ ) showed a single very strong band at  $250\text{ cm}^{-1}$  which, in line with its increased width (ca.  $30\text{ cm}^{-1}$ ), can be attributed to amorphous Se [4,5]. FTIR spectra of the purified Se NPs showed the presence of capping biomacromolecules (proteins, polysaccharides, as well as lipids featured by increased C–H stretching modes as compared with FTIR spectra of bacterial biomass). Relative contents of proteins and polysaccharides in the capping layer of the Se NPs noticeably differed for the two strains. It was also found that, in comparison with the earlier data [2], the amount of carboxylic moieties contained in biomacromolecular ‘shell’ can be noticeably decreased by washing, so that they are relatively loosely bound to the Se NPs surface, in contrast to the biomacromolecular ‘shell’ itself. The Se NPs were also characterised by dynamic light scattering (DLS), UV-Vis spectrophotometry and transmission electron microscopy (TEM). Thus, a combination of FTIR and Raman spectroscopic approaches is highly informative in non-destructive analysis of structural and compositional properties of biogenic Se NPs, which differ even for bacteria of the same genus and can be controlled by modifying the procedures of their bacterial synthesis and purification. **Acknowledgement.** This study was supported in part by The Russian Foundation for Basic Research (Grant 16-08-01302-a). [1] A.V. Tugarova, E.P. Vetchinkina, E.A. Loshchinina, A.M. Burov, V.E. Nikitina, A.A. Kamnev. *Microb. Ecol.* 68 (2014) 495-503. [2] A.A. Kamnev, P.V. Mamchenkova, Yu.A. Dyatlova, A.V. Tugarova. *J. Mol. Struct.* (2017) DOI: 10.1016/j.molstruc.2016.12.003. [3] K. Lavrinenko, E. Chernousova, E. Gridneva, G. Dubinina, V. Akimov, J. Kuever, A. Lysenko, M. Grabovich. *Int. J. Syst. Evol. Microbiol.* 60 (2010) 2832-2837. [4] G. Lucovsky, A. Mooradian, W. Taylor, G.B. Wright, R.C. Keezer. *Solid State Commun.* 5 (1967) 113-117. [5] O. Van Overschelde, G. Guisbiers. *Opt. Laser Technol.* 73 (2015) 156-161.



## Characterization of the Aggregation Mechanism of Amyloid- $\beta$ peptides with $\text{Cu}^{2+}/\text{Zn}^{2+}$ Using Fluorescence Correlation Spectroscopy

Qian Wang<sup>A</sup> and Yun-Bao Jiang<sup>A\*</sup>

<sup>A</sup>Department of Chemistry, College of Chemistry and Chemical Engineering, the MOE Key Laboratory of Spectrochemical Analysis and Instrumentation, and the Collaborative Innovation Centre of Chemistry for Energy Materials (iChEM), Xiamen University, Xiamen 361005, China

[wqchem@xmu.edu.cn](mailto:wqchem@xmu.edu.cn)

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**ABSTRACT:** Alzheimer's disease (AD) is the most common cause of dementia and one of the major hallmarks of AD is the progressive deposition of A $\beta$  protein fragments into  $\beta$ -sheet rich amyloid fibrils in excellular neuron cells. Extensive studies on A $\beta$  have indicated that the most neurotoxic forms of A $\beta$  aggregation forms are small oligomers rather than the A $\beta$  fibrils in the late aggregation stages. Metal ions, such as copper and zinc, have been implicated in the pathogenesis of Alzheimer's disease through a variety of mechanisms including increased amyloid- $\beta$  affinity and redox effects. The exact mechanism of the A $\beta$ , together with metal ions aggregation process remains unclarified. Fluorescence correlation spectroscopy (FCS) is a correlation analysis of fluctuation of the fluorescence intensity, which allows the analysis of dynamic processes in biological systems with extremely high temporal and spatial resolution and minimal disturbance to the system. In this study, we applied FCS as well as multiple ensemble and single molecule level investigations to characterize the aggregation kinetics and secondary structure change of A $\beta$  in the absence and the presence of  $\text{Cu}^{2+}$  or  $\text{Zn}^{2+}$ . Our results indicated that, (1) the A $\beta$ (1-42) peptide was aggregated through two distinct pathways, one leading to long amyloid fibrils and the other to relatively stable oligomers; (2) with the presence of different concentrations of  $\text{Cu}^{2+}$  or  $\text{Zn}^{2+}$ , the secondary structure and aggregation kinetics of A $\beta$ (1-42) aggregates was induced from  $\beta$ -sheet rich amyloid fibrils into amorphous peptide-metal complexes; (3) the  $\text{Cu}^{2+}$  or  $\text{Zn}^{2+}$  : A $\beta$  stoichiometry affected the kinetic scenario of A $\beta$ (1-42) aggregation process. Particularly, subequimolar ratios of  $\text{Cu}^{2+}$  or  $\text{Zn}^{2+}$  increased the size of A $\beta$ (1-42) oligomers. This research provides correlated analysis of A $\beta$ (1-42) aggregation kinetics in the presence of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  at single molecule level, together with the secondary structure change of the peptide, which provides a much more comprehensive understanding of A $\beta$  aggregation mechanism and cytotoxicity.

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## Study of selectivity of Nanoparticle Enhanced Laser-Induced Breakdown Spectroscopy signal enhancement

Lucia Sládková<sup>\*A</sup>, Pavel Pořízka<sup>A, B</sup>, Jakub Klus<sup>A, B</sup>, Pavlína Škarková<sup>A</sup>, David Prochazka<sup>A, B</sup>,  
Michaela Remešová<sup>A</sup>, Karel Novotný<sup>A</sup>, Ladislav Čelko<sup>A</sup>, Jozef Kaiser<sup>A, B</sup>

<sup>A</sup>CEITEC - Central European Institute of Technology, Brno University of Technology, Purkyňova 123,  
612 00 Brno, Czech Republic; <sup>B</sup>AtomTrace, a.s., Kolejní 9, 616 00 Brno, Czech Republic

\*lucia.sladkova@ceitec.vutbr.cz

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**ABSTRACT:** *In the Nanoparticle Enhanced Laser-Induced Breakdown Spectroscopy (NELIBS) experiment nanoparticles applied on the studied sample surface increase detected signal and improve limits of detection. It was already shown that the enhancement of detected signal in NELIBS is selective, i.e. occurs only for certain emission lines in whole measured spectral range, and is strongly affected by the quantum parameters, plasma temperature etc. In this work we investigated selectivity from two aspects: i) its dependency on the emissions line central wavelength and ii) level of enhancement. The focus was given namely to quantum properties of individual emission lines (values of upper energy levels and Einstein coefficients) of minor and trace elements in the measured spectral range.*

*The plasma temperature identified from the Saha-Boltzmann equation and the electron density were studied also. Both with the connection to the selectivity and enhancement level of chosen emission lines. This was performed with the purpose to characterize the enhancement effect in detail. NELIBS measurements were performed on different metallic alloys with the spherical silver nanoparticles applied on the sample surface. To evaluate the enhancement selectivity phenomena thoroughly, both minor and trace elemental emission lines were chosen for the analysis.*

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## Control of the depth resolution and crater diameter in elemental depth profiling based on laser ablation

Juri Agresti<sup>\*A</sup>, Salvatore Siano<sup>A</sup>

<sup>A</sup>Istituto di Fisica Applicata “Nello Carrara”-CNR, 50019 Sesto Fiorentino (FI), Italy.

<sup>\*</sup>j.agresti@ifac.cnr.it

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**ABSTRACT:** Compositional depth profiling represents one of the main analytical advantages of laser-ablation based spectroscopic techniques such as laser induced plasma/breakdown spectroscopy (LIPS/LIBS) and laser ablation inductively coupled plasma emission or mass spectroscopy (LA-ICP-ES or LA-ICP-MS). These techniques can play a crucial role for addressing several material characterization problems involving multilayered microstructures. On the other hand, when they are used in order to achieve elemental depth profiles through relatively thick superposition of strata (depth much larger than the laser spot), complex crater shape transformations are observed during the measurement, which determine substantial changes on the actual analytical depth resolution. In particular, significant increases of the crater diameter have been reported in both LIPS and LA-ICP applications above a given aspect ratio threshold. However, so far, experimentally supported models providing satisfactory descriptions of such a phenomenon and of the associated changes in depth resolution is still missing. Here, the phenomenological results have been successfully compared with an interpretative scheme based on the modelling of the temporal evolution (while releasing the laser pulse sequence to the target) of the laser propagation through the plasma region. We show that a simplified analytical model using geometric optics can allow interpreting the experimental data of the depth profile resolutions and crater size/shape evolutions. The observed trends of crater-shapes and elemental signals during LIPS depth profiling of metal samples are discussed according to the pulse energy redistribution due to laser-crater-plasma interactions, as evaluated by means of optical simulations. Spectral emission and depth profiles have been correlated with the associated variations of ablation rates and crater shape parameters, in order to derive a general optimization criterion for maximizing the resolution of elemental depth profiles.

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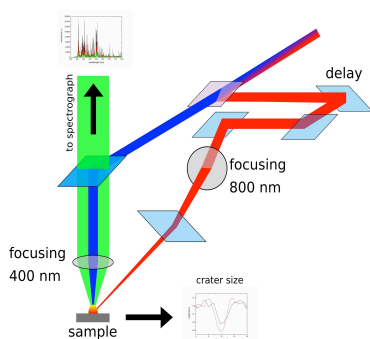
## On the emission enhancement in dual-pulse femtosecond laser-induced breakdown spectroscopy of metals

Christoph M. Ahamer <sup>\*A</sup>, Kevin M. Riepl <sup>A</sup>, Norbert Huber <sup>A</sup>, Johannes D. Pedarnig <sup>\*A</sup>

<sup>A</sup> Institute of Applied Physics, Johannes Kepler University, Altenberger Straße 69, 4040 Linz, Austria

\* christoph.ahamer@jku.at

**ABSTRACT:** This work aims to investigate the emission enhancement in dual-pulse femtosecond laser-induced breakdown spectroscopy (LIBS). We discuss line intensity enhancement mechanisms and possible applications of femtosecond dual-pulse LIBS for imaging with high spatial resolution. The fundamental radiation of a Ti:sapphire femtosecond laser ( $\lambda = 800$  nm,  $t \approx 175$  fs,  $f_{rep} = 1$  kHz) was frequency-doubled with a BBO crystal ( $\lambda = 400$  nm) and the 400 nm and 800 nm beams were spatially separated by a dichroic mirror. The 400 nm pulse was focused under perpendicular incidence on the sample (biconvex lens of focal length  $f_1 = 15$  mm) and ablated material from the sample surface (crater diameter  $d \geq 2$   $\mu$ m). The 800 nm pulse was delayed about 300 ps with respect to the ablation pulse and focused ( $f_2 = 200$  mm) on the sample under oblique incidence ( $\sim 45^\circ$ ). The inter pulse delay was chosen in order to obtain stable plasma conditions with optimum signal enhancement [1][2]. Plasma was induced on metal bulk and thin film samples and the optical emission spectra were measured in collinear geometry using an Echelle spectrometer and ICCD camera for broadband and time-resolved detection. We measured emission line intensities, plasma temperature  $T_e$ , and electron number density  $N_e$  in dependence of the energy of the two fs laser pulses and the detection delay time. Strongest dual-pulse enhancement of Cu line intensities (up to 25 $\times$ ) is observed at low energy of the ablation pulse. Similarly, the volume of dual-pulse ablation craters increases at low energy of the ablating pulse (up to 10 $\times$ ). The time-resolved plasma parameters  $T_e$  and  $N_e$  are very close for single-pulse (400 nm) and dual-pulse (400 nm + 800 nm) excitation. Our results indicate that femtosecond dual-pulse signal enhancement on metals is mainly due to an increased ablation rate rather than to plasma re-heating effects. Figure 1: Illustration of fs dual pulse experiments. [1] V. Piñon et al., Double pulse laser-induced breakdown spectroscopy with femtosecond laser pulses, *Spectrochimica Acta Part B: Atomic Spectroscopy*, Volume 63, Issue 10, October 2008, Pages 1006-1010 [2] Wang et al., Enhancement of laser-induced Fe plasma spectroscopy with dual-wavelength femtosecond double-pulse, *J. Anal. At. Spectrom.*, 2016, 31, 497-505 Acknowledgements: Financial support by the Austrian Research Promotion Agency FFG (imPACts Project 843546) is



*gratefully acknowledged.*

## Chromium speciation using Magnetic magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles synthesized by coprecipitation method and detection by FAAS.

Vanessa Nunes Alves<sup>\*A</sup>, Carolina A. de S. Silva<sup>A</sup>

<sup>A</sup>Chemistry Department, Federal University of Goiás, Av. Lamartine Pinto de Avelar, 1120, Catalão, Brazil.

<sup>\*</sup>vanessanalves@gmail.com

**ABSTRACT:** Among the metals largely used for industrial purposes, special attention should be given to chromium, which is used in a number of industrial. Chromium is found in its two most stable oxidation states of Cr(VI) and Cr(III), which have different toxicity, mobility and bioavailability. Cr(VI) is known to be toxic to both plants and animals as well as potentially being carcinogenic, while Cr(III) as essential to human<sup>1</sup>. So, it is essential to develop analytical methods for quantifying the targeted two forms and the use of prior extraction and/or preconcentration step of the sample can aid in improving chromium determination by spectroscopy methods. Solid phase extraction (SPE) based on the selective or simultaneous retention of Cr(III) and Cr(VI) sorbents is the most widely employed procedures for the chromium speciation<sup>2</sup>, but magnetic solid phase extraction (MSPE) has been used successfully in various preconcentration procedures. Magnetic nanoparticle, as a new kind of nanometer-sized material, is widely used in the fields of chemistry and medicine. Use of them have become increasingly popular for the development of magnetic extraction methods due to the advantages of easy control and simple separation, once these particles can be collected by an external magnetic field. In this context, this work evaluates the use of magnetite to speciation of chromium ions and detection by FAAS. Magnetite nanoparticles were prepared by coprecipitation method. In brief, a solution containing  $\text{FeSO}_4$  and  $\text{FeCl}_3$  in  $\text{H}_2\text{O}$  was prepared and acidified with  $\text{HCl}$ . The ions were dissolved with stirring, and the solution has resulted in a precipitated by the  $\text{NH}_4\text{OH}$  addition. Synthesized particles were decanted magnetically by a magnet, filtered, washed with water and dried in an oven. The aqueous pH affect significantly metal ion adsorptions, influencing surface chemistry, determining the adsorbent surface charge and the degree of ionization, and speciation the adsorbed species<sup>3</sup>. The effect of pH solution on the Cr(VI) and Cr(III) separation was investigated by varying the pH from 1 to 12. So, the pH was adjusted by adding  $0.1 \text{ mol L}^{-1} \text{HNO}_3$  or  $0.1 \text{ mol L}^{-1} \text{NH}_4\text{OH}$ . Twenty-five milliliters of a solution containing separately each species were placed under stirring with  $0.0065 \text{ g}$  of magnetite for 1 hour, after there was a magnetic separation and the concentration of chromium species was measured in supernatant, and retained amount of chromium in magnetite was calculated by the difference between the initial and final concentrations. The Cr(VI) ions have a maximum adsorption at pH 3, while the trivalent species has your maximum adsorption at pH 8-9, in which the hexavalent species adsorption is rarely observed. In aqueous systems, the surface of iron oxides is covered with  $\text{FeOH}$  groups. Surface hydroxyl groups protonate or deprotonate to generate surface charge  $\text{FeOH}_2^+$  or  $\text{FeO}^-$  functions at pH values below or above the  $\text{pH}_{\text{pzc}}$ . Magnetite's zero point charge is the pH value at which the surface concentration of  $\text{FeOH}_2^+$  and  $\text{FeO}^-$  are equal. The measured  $\text{pH}_{\text{pzc}}$  (9.2) of magnetite surface is close to neutral. High Cr(VI) adsorption occurs in the lower pH acidic range where magnetite's surface has a net positive charge from  $\text{FeOH}_2^+$  and Cr(VI) species are negative ( $\text{Cr}_2\text{O}_7^-$ ,  $\text{HCrO}_4^-$ ). Increasing pH leads to a decrease in Cr(VI) adsorption, since as surface  $\text{FeOH}_2^+$  sites are increasingly converted to  $\text{FeO}^-$ , electrostatic attractions to anionic chromium species drop and repulsions increase. In contrast, the electrostatic attractions between  $\text{FeO}^-$  and Cr(III) species ( $\text{Cr}(\text{OH})_2^+$ ). Thus, Cr(VI) can be separated when the initial pH of the solution is in the range of 1-3, while the Cr(III) can be separated when the initial pH of the solution is between 8 and 9. [1] C.R. Myers, J.M. Myers, B. P. Carstens, W. E. Antholine. Toxic Subst. Mech 19(2000)25-51 [2] V.N. Alves, N. M. M. Coelho. Microchemical journal 109 (2013)16-22 [3] D. Mohan, H. Kumar, A. Sarwast, M. Alexandre-Franco, C. U. Pitmtman Jr. Chem. Eng. J. 236 (2014) 513-517

## Application of WDXRF analysis for paleoclimatic investigations

Alena Amosova\*, Victor Chubarov

Vinogradov Institute of Geochemistry, Siberian Branch of Russian Academy of Sciences,  
1A Favorsky st., Irkutsk, Russian Federation

\*alena\_amosova@mail.ru

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**ABSTRACT:** The basis for investigation of the total and regional past climatic and environmental changes is the precise determination of the elemental composition of bottom sediments. The concentrations of major elements accumulated in sedimentary records over longer time periods are used to track possible causes, timing and intensity of weathering processes in the lake catchment areas. Small material mass (less than 300 mg) is the main difficulty in bottom sediments core analysis. We developed X-ray fluorescence technique using only 110 mg of sample for quantitative analysis and used it for analysis of 143 cm-long core from the lake Baunt (Republic of Buryatia, Russian Federation). The mineralogy of the terrigenous component was studied by X-ray powder diffraction analysis. Ten certified reference materials of sedimentary rocks were utilized for estimation of reproducibility of sample preparation, measurement and for calibration curves construction. Homogenization by the fusion with lithium metaborate in platinum crucibles in electric fluxer at 1050 °C was employed to eliminate the influence of mineral and grain-size composition. Obtained discs up to 10-12 mm in diameter were analyzed on wavelength-dispersive X-ray fluorescence spectrometer S8 Tiger equipped with Soller optical system, X-ray tube with Rh anode and collimator mask 8 mm. To account matrix effects the fundamental parameter method was applied. Results of major rock-forming oxides determination ( $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ ,  $\text{MnO}$  and  $\text{Fe}_2\text{O}_3$ ) were compared with the data of spectrophotometry and flame photometry techniques, results of Sr and Zr determination were compared with the data of synchrotron radiation excited X-ray fluorescence technique. Relative standard deviation of analytical results corresponds to requirements of quantitative analysis and do not exceed 3 % for major oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ) and 10% for other elements. Obtained element concentrations, its ratios and calculated climatic modules represent sedimentation conditions triggered by environmental and climate changes such as chemical changes in lacustrine sediments, relative chemical weathering intensity and degree of sediment maturity. Quantitative analysis of the each centimeter of Lake Baunt sediment core allowed building first reconstructions of the local environment during last 7000 years with unique resolution about 100 years. X-ray fluorescence analysis is carried out by the financial support by Russian Science Foundation (project № 16-17-10079). Drilling expeditions, spectrophotometry and flame photometry analyses were carried out by the financial support of the Russian Foundation for Basic Research (projects № 15-05-01644 and № 16-35-00235). Measurements were performed using equipment of the joint use centers (Geodynamics and Geochronology Center, Isotope-geochemical Research Center and Siberian Synchrotron and Terahertz Radiation Centre).

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## Geochemical characteristic of bottom sediments using X-ray fluorescence spectra

Alena Amosova\*, Victor Chubarov

Vinogradov Institute of Geochemistry, Siberian Branch of Russian Academy of Sciences,  
1A Favorsky st., Irkutsk, Russian Federation

\*alena\_amosova@mail.ru

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**ABSTRACT:** Climate changes largely determine the lake sedimentation at the regional scope. The data on the landscape and climatic conditions derived from geochemical and palynological investigations present valuable information about environment and climate changes. 143 cm-long bottom sediments core from the lake Baunt (Republic of Buryatia, Russian Federation) was analyzed on a wavelength-dispersive X-ray fluorescence spectrometer S8 Tiger by technique using fusion preparation that enables to analyze small weight (110 mg) samples. The proposed technique allows determining major rock-forming and some microelements (Sr, Zr) in the bottom sediments with the analyzed material shortage. High correlation coefficients between  $Al_2O_3$ ,  $K_2O$ ,  $MgO$  and  $TiO_2$  (0.89-0.93),  $SiO_2$  and  $Al_2O_3$  (-0.69),  $SiO_2$  u  $Fe_2O_3$  (-0.65),  $CaO$ ,  $Na_2O$  and  $Al_2O_3$ ,  $K_2O$ ,  $MgO$ ,  $TiO_2$  (0.65-0.71) can be explained by the mineral composition presented by Na, K and Mg aluminosilicates with Fe and Ca impurities. High correlation coefficient between  $P_2O_5$  and  $MnO$  (0.90) with high iron content in some samples can be explained by the presence of mineral vivianite, that corresponds to lakes Baikal and El'gygytyn data. Quantitative determination of those elements is the basis for estimation of important ratios and climatic modules, representing sedimentation conditions triggered by environmental and climate changes such as chemical changes in lacustrine sediments, relative chemical weathering intensity and degree of sediment maturity. We assessed varying of climatic modules: chemical index of alteration (from 71.7 to 74.5), chemical index of weathering (from 79.5 to 83.4), the plagioclase index of alteration (from 76.9 to 81.1) and chemical proxy of alteration (from 87.0 to 91.6). High correlation coefficients (0.86-0.96) are observed between all these indexes. The varying of titanium module (from 8.6 to 9.7), aluminosilicate module (from 0.2 to 0.3) and the ratio of Zr and Sr concentrations (from 0.33 to 0.45) were also calculated. Combination of obtained high-resolution geochemical and pollen records from Baunt Lake was used to derive characteristics of the weathering natural conditions in the catchment area of the lake. Analysis of sediments with average time resolution of about 100 years provided an excellent opportunity for reconstructing the regional climate and landscapes throughout the Middle-Late Holocene. X-ray fluorescence analysis is carried out by the financial support by Russian Science Foundation (project № 16-17-10079). Drilling expeditions and X-ray diffraction were carried out by the financial support of the Russian Foundation for Basic Research (projects № 15-05-01644 and № 16-35-00235). Measurements were performed using equipment of the joint use centers (Geodynamics and Geochronology Center, Isotope-geochemical Research Center and Siberian Synchrotron and Terahertz Radiation Centre).

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## Antarctic Environmental Specimen Bank: A playground for analytical spectroscopists

Francisco Ardini\*, Andrea Bazzano, Francesco Soggia, Marco Grotti

Department of Chemistry and Industrial Chemistry, University of Genoa, Via Dodecaneso 31, Genoa, Italy.

\*ardini@chimica.unige.it

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*ABSTRACT: Environmental Specimen Banks (ESBs) are facilities that archive samples from the environment for future research and monitoring purposes. The samples are collected using validated procedures and stored under well-defined preservative conditions, so that they can be used to analyze temporal trends of known hazardous substances, previously unrecognized pollutants, or chemical species of environmental interest for which analytical techniques were inadequate at the time of sampling. Therefore, ESBs are valuable resources of specimens for real-time and retrospective monitoring purposes, as well as to test new analytical methods and techniques. In the past 20 years, the Antarctic ESB have supported many environmental projects, and concurrently stimulated a great deal of research in the analytical chemistry field, in order to face the challenges related to the ultra-trace analysis of polar matrices. In particular, a number of studies concerned the elemental, speciation and isotopic analysis of environmental samples (atmospheric particulate, surface snow, marine organisms, sea-water and sea-ice) using plasma source atomic emission and mass spectrometry, atomic absorption spectrometry and hyphenated techniques. In this presentation, representative examples of ESB-based studies involving the spectrochemical analysis of Antarctic samples are presented and discussed. It is shown how the analytical needs arising from these investigations stimulated the development of new analytical methods and how the developed methods successfully provided valuable information for the study of the Antarctic environment.*

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## Determination of Various Minerals in Rice Samples Sold in Turkey using microwave induced plasma optical emission spectrometry

Ece Atespare<sup>A</sup>, Nil Ozbek<sup>A</sup>, Hande Tinas<sup>A</sup>, Suleyman Akman<sup>A</sup>

<sup>A</sup> Department of Chemistry, Istanbul Technical University, Maslak, Istanbul, Turkey.

atespare@itu.edu.tr

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**ABSTRACT:** Rice is one of the most common food for the most of the world. It is an important source of energy, vitamins, amino acids, minerals and other nutrients for humans. The mineral content of rice is highly influenced by the degree of polishing/milling and the contents of mineral elements in rice are closely related to public health. Due to its large consumption, the accurate determination of the elemental composition of rice is of utmost importance for estimating the population's dietary intake of nutrients and their exposure to toxic elements. In this study, a practical method was described to determine various elements in different rice samples using microwave induced plasma optical emission spectrometry (MIP OES). Prior to analysis, rice samples were dried at 110°C overnight then ground using an agate mortar. The powdered rice samples and standard reference material were weighted around 0.1 g and digested using 10 mL HNO<sub>3</sub> till clear digests were obtained. To be on safe side, digests then filtered through and then directly aspirated to the plasma. All determinations were performed using aqueous standards for calibration. The LOD values for were calculated. The analytes in certified reference material was determined in the uncertainty limits of the certified values as well as the analytes added to the samples prior to digestion were recovered quantitatively (> 90%). No spectral interference was detected at the working wavelengths of the analytes. Finally, the analyte concentrations in various types of rice samples were determined.

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## Simultaneous Determination of Copper, Iron, Chromium, Lead, Manganese, Magnesium, Nickel and Sodium in Chocolate Samples by Flame Atomic Absorption Spectrometry After Extraction Induced by Emulsion Breaking

Dilek Bakircioglu<sup>\*A</sup>, Nukte Topraksever<sup>A</sup>, Anil Gogercin<sup>A</sup>, Yasemin Bakircioglu Kurtulus<sup>A</sup>

<sup>A</sup>Department of Chemistry, University of Trakya, Edirne, Turkey.

\*dbakircioglu@trakya.edu.tr

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**ABSTRACT:** Chocolates especially stimulate the potential stimulants, relaxants and antidepressants that give joy and pleasure to children [1,2]. The main components of chocolate are cocoa butter, chocolate liquor and sugar. However, the composition of the chocolate depends on the product. While dark colored chocolates with a high degree of cocoa are generally considered a good source of magnesium and copper, milky and white chocolates are a good source of calcium [3]. Excessive consumption of confectionery products with it causes incidences of type 2 diabetes, obesity and tooth decay [4]. Particularly cocoa-containing foodstuffs, cause high levels of nickel, chromium and lead contamination, posing a threat to human health [5]. Chocolate is a complex sample with a high content of organic compounds, and its analysis usually involves digestion procedures (dry, wet and microwave digestion) that could pose the risk of sample loss and contamination. In this study, a novel and highly sensitive method based on induced by emulsion breaking, is proposed for rapid simultaneous determination of copper (Cu), iron (Fe), chromium (Cr), lead (Pb), manganese (Mn), magnesium (Mg), nickel (Ni) and sodium (Na) in chocolate samples by flame atomic absorption spectrometry. This method is simpler and requires fewer reagents when compared with other sample pre-treatment procedures and allows the calibration to be carried out using aqueous standards. The emulsions were prepared by mixing the melted chocolate samples (3 gram) diluted in toluene with 7% m/v Triton X-114 solution in 10% v/v HNO<sub>3</sub>. The emulsion breaking was performed by heating at 80± 2 °C following by centrifugation to improve the separation, resulting in two distinct phases. The aqueous phase was analyzed by FAAS using inorganic standards solutions for external calibration. Cu, Fe, Cr, Pb, Mn, Mg, Ni and Na were totally extracted at a single extraction step. [1] M. Macht, J. Mueller, *Appetite* 49 (2007) 667–674 [2] G. Parker, I. Parker, H. Brotchie, *Journal of Effective Disorder* 92 (2006) 149–159 [3] F.M. Steinberg, M.M. Bearden, C.L. Keen, *Journal of the American Dietetic Association* 103 (2003) 215–223 [4] G.H. Anderson, *Nutritional Research* 17 (1997) 1485–1498 [5] S. Dahiya, R. Karpe, A.G. Hegde, R.M. Sharma, *Journal of Food Composition and Analysis*, 18 (2005) 517–522.

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## A Novel, Rapid and Simple Extraction Induced by Emulsion Breaking Procedure for Cu, Mn and Ni Determination in Margarine

Yasemin Bakircioglu Kurtulus<sup>\*A</sup>, Alper Can Babac<sup>A</sup>, Dilek Bakircioglu<sup>A</sup>

<sup>A</sup>Department of Chemistry, University of Trakya, Edirne, Turkey.

\*ybakircioglu@trakya.edu.tr

**ABSTRACT:** The metal content of margarine is an important indicator of their quality [1]. The amount of metals in the oil can be related both to the environment and to oil processing and storage conditions [2]. Oil and fats can cause spectral interferences due to the formation of nearly totally organic matter, which leads to time-consuming sample mineralization procedures for sensitivity improvements [1]. Procedures such as extraction, preconcentration and acid digestion have been used to reduce the effect of the organic matrix. For this reason, although there are many studies on the determination of trace elements in oil samples, this work area is not yet complete [3].

The purpose of this study is to suggest a new strategy for preparation of induced by emulsion breakdown procedure prior to determination of copper, manganese and nickel in margarine samples by graphite furnace atomic absorption spectrometry (GF-AAS). Several parameters affecting the performance of the procedure such as oil phase: aqueous phase ratio, type and concentration of surfactant, concentration of HNO<sub>3</sub>, temperature were investigated. Total quantitative extraction of Cu, Mn, and Ni could be achieved when 4 g of margarine sample was emulsified in 2 mL of 7 % Triton X-114 (in % 10 HNO<sub>3</sub>). The emulsion obtained under these conditions was broken at 80 °C. The studied metal content in the separated aqueous phase was analyzed by GF-AAS using inorganic standard solutions for external calibration. The accuracy of the proposed procedure was tested by comparison with the reference procedure based on the total digestion of the samples in microwave acid digestion procedure and by spiking the samples with known concentration of Cu, Mn and Ni, added as organometallic oiled standard. [1] A. Zhuravlev, A. Zacharia, S. Gucer, A. Chebotarev, M. Arabadji, A. Dobrynin, *Journal of Food Composition and Analysis* 38 (2015) 62–68 [2] Roseli M. de Souza, Barbara M. Mathias, Carmem Lucia P. da Silveira, Ricardo Q. Azeiteiro, *Spectrochimica Acta Part B* 60 (2005) 711 – 715 [3] Alex M. Trevelin, Rubia E.S. Marotto, Eustaquio V.R. de Castro, Geisamanda P. Brandao, Ricardo J. Cassella, Maria Tereza W.D. Carneiro, *Microchemical Journal* 124 (2016) 338–343

## The examination of iron and manganese retention in the aquatic food chain by atomic spectrometric methods

Petra Herman<sup>A</sup>, Sándor Harangi<sup>A</sup>, Milán Fehér<sup>B</sup>, Edina Baranyai <sup>\*A</sup>

<sup>A</sup>Agilent Atomic Spectroscopy Partner Laboratory, Department of Inorganic and Analytical Chemistry,  
University of Debrecen, Debrecen H-4010, Hungary

<sup>B</sup>Department of the Agricultural and Food Sciences and Environmental Management, University of Debrecen,  
Debrecen H-4032, Hungary

\*baranyai.edina@science.undideb.hu

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**ABSTRACT:** Metal contamination in aquatic environment has attracted global attention recently. Bacteria, zooplankton and fish represent different trophic levels in the food chain and indicate the quality of the surrounding water. In our research we investigate the accumulation extent of the inorganic contaminants accessing the aquatic food chain (including zooplankton and fish species). In the preliminary experiments the zooplankton organisms are reared in contaminated model media and the accumulated concentrations of elements are measured from their tissues providing information about the extent of pollution. The retention of two elements (Mn and Fe) was studied in one salt water (*Artemia nauplii*) and in one freshwater (*Daphnia pulex*) zooplankton species. We applied five treatments with different concentrations of these trace minerals and after the 24 hours enrichment period the accumulation of the elements were analysed by two atomic spectrometric methods (MP-AES and ICP-OES). In case of *Artemia* the concentration of Mn increased in parallel with the dose of the supplementations. Opposite this, examining the Fe concentrations in the five treatments there were no significant difference. Based on the results, *Daphnia* amass iron and manganese more effectively, than *Artemia*. The level of both elements increased in parallel with the dose of the supplementations in the freshwater organisms. This research proves that these creatures are able to effectively accumulate inorganic nutrients and pollutants in their body. Thus, by serving them as resource for consumers on higher trophic levels (including fish), the accumulation through live food can be determined.

**ACKNOWLEDGMENTS:** Petra Herman was supported through the ÚNKP-16-2-I New National Excellence Program of the Ministry of Human Capacities. The research was supported by the EU and co-financed by the European Regional Development Fund under the project GINOP-2.3.2-15-2016-00008. We would like to highly acknowledge the Agilent Technologies and the Novo-Lab Ltd. (Hungary) for providing the MP-AES 4200 and the ICP-OES 5100.

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## Trace element determination of tree sap by microwave plasma atomic emission spectrometry

Henriett Kiss<sup>A</sup>, Sándor Harangi<sup>A</sup>, Edina Baranyai<sup>\*A</sup>

<sup>A</sup>Agilent Atomic Spectroscopy Partner Laboratory, Department of Inorganic and Analytical Chemistry,  
University of Debrecen, Debrecen H-4010, Hungary

\*baranyai.edina@science.undideb.hu

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*ABSTRACT: Tree sap is the fluid responsible to transport water and essential nutrients throughout the plant. There are countries where the early spring sap is harvested of some species for human consumption: from the commodity of beers, wine or honey to the folk medicinal use. However, plant can accumulate toxic elements and substances from the soil and air that can have adverse health effects. The aim of this study is to determine the mineral content and elemental contamination of tree sap originating from different species and areas of Hungary. Atmospheric and microwave-assisted digestion was compared to find the most suitable sample preparation process. The elemental concentration of sap samples was determined by MP-AES method and the results were verified by ICP-OES technique. Statistical analysis was used to evaluate the data. Results showed that the microwave-assisted digestion was more efficient and the more cost effective MP-AES method proved to be appropriate for the trace element analysis of tree sap. Significant difference occurred among the sampling locations and tree species regarding the elemental composition. Acknowledgement: The research was supported by the EU and co-financed by the European Regional Development Fund under the project GINOP-2.3.2-15-2016-00008. We would like to highly acknowledge Agilent Technologies (Novo-Lab Ltd.) for providing the MP-AES 4200 and ICP-OES 5100 instrument for the elemental analysis.*

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## Determination of antimony and tin in beverages using inductively coupled plasma-optical emission spectrometry after ionic liquid based ultrasonic-assisted liquid-liquid phase microextraction

N. Raphael Biata<sup>a</sup>, Luthando Nyaba<sup>a</sup>, James Ramontja<sup>a</sup>, Nomvano Mketo<sup>b</sup>, Philiswa N. Nomngongo<sup>a1</sup>

<sup>a</sup>Department of Applied Chemistry, University of Johannesburg, Doornfontein Campus, P.O. Box 17011, Johannesburg, 2028, South Africa

<sup>b</sup>Analytical Facility, University of Johannesburg, P.O. Box: 524, Auckland Park 2006, South Africa

pnnomngongo@uj.ac.za

**ABSTRACT:** A simple, fast and environmentally friendly ligandless preconcentration technique based on ultrasonic-assisted ionic liquid - liquid-liquid phase microextraction (UA-IL-LLME) has been developed and used for analysis of trace antimony and tin in different beverage samples. The IL (Aliquat 336) was dissolved in *n*-butyl acetate and used as a low density hydrophobic extractant solvent. The quantification of trace-metals was carried-out using inductively coupled plasma-optical emission spectrometry for simultaneous determination of Sb and Sn in various beverages. Under the optimum conditions, the calibration graph was linear over the range of LOQ-250  $\mu\text{g L}^{-1}$  ( $r^2 = 0.9987$ ) for Sb and LOQ- 350  $\mu\text{g L}^{-1}$  ( $r^2 = 0.9991$ ) for Sn. The LOD and LOQ ( $n=10$ ) were found to be 2.5  $\text{ng L}^{-1}$  and 8.3  $\text{ng L}^{-1}$  for Sb and 1.2  $\text{ng L}^{-1}$  and 4.0  $\text{ng L}^{-1}$  for Sn, respectively, with high preconcentration factors (250, Sb and 275, Sn). The precisions [intraday (repeatability;  $n = 15$ ) and interday (reproducibility;  $n = 7$  working days)] of the proposed UA-IL-LLME method, expressed in terms of relative standard deviation (% RSD) at 50.0  $\mu\text{g L}^{-1}$  ranged from 2.1-2.5% and 3.9-4.7% for Sb and Sn, respectively. The effect of coexisting ions in the extraction and preconcentration of Sb and Sn in the real samples were investigated. The proposed method was successfully applied for determination of Sb and Sn in different nonalcoholic beverage samples. The analytical results of the developed method were in good agreement with those obtained using reference method and good spiked average recovery of 98.3% was obtained.

## Measurement of Laser Generated Plasma Parameters through the Perturbation caused by the plasma in a stationary electric field

Fausto Bredice<sup>\*A</sup>, Citlali Sánchez-Aké<sup>B</sup>, Mayo Villagrán Muniz<sup>B</sup>, Vincenzo Palleschi<sup>C</sup>  
Paola Pacheco Martínez<sup>D</sup>, R. Sarmiento Mercado<sup>D</sup>

<sup>A</sup> Centro de Investigaciones Ópticas (CIOP), C.C.3, 1897, Gonnet, La Plata, Argentina

<sup>B</sup> Laboratorio de Fotofísica, Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México, Apartado Postal 70-186, Cd. Mx. 04510, México

<sup>C</sup> Institute of Chemistry of Organometallic Compounds Research Area of National Research Council, Via G. Moruzzi, 1 – 56124 Pisa, Italy

<sup>D</sup> Grupo de Espectroscopía Óptica de Emisión y Láser, (GEOEL), Universidad del Atlántico, Km 7 Vía a Puerto Colombia, Barranquilla, Colombia

\*faustob@ciop.unlp.edu.ar

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*ABSTRACT: When laser-induced plasma is placed between the plates of a planar charged capacitor, the plasma generates a transient redistribution of the electrical charges on the plates that can be easily measured as a voltage drop across a resistor connected to the ground plate (1). This signal is proportional to the capacitor applied voltage, the distance between the plates and the total number of ions removed by breakdown which in turn is related to the laser energy deposited in the breakdown process and the electron density of the plasma. Moreover, this method can be applied for characterization of breakdown in gas or ablation of solid targets. In this work we show that the electrical signal measured on the resistor is univocally related to the consumed energy during the breakdown process, the electron density of the plasma and the ablated mass from the target. Therefore, after a proper calibration depending on the material and the experimental geometry, the peak of the electrical signal can be used for real time quantitative measurement of the above mentioned parameters in pulsed laser generated plasma experiment.*

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## Temporal Evolution of the Boltzmann Plot as a Tool for the Characterization of Plasma Generated by Laser

Fausto Bredice<sup>\*A</sup>, Citlali Sánchez-Aké<sup>B</sup>, Mayo Villagrán Muniz<sup>B</sup>,

<sup>A</sup> Centro de Investigaciones Ópticas (CIOP), C.C.3, 1897, Gonnet, La Plata (Argentina)

<sup>B</sup> Laboratorio de Fotofísica, Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México, Apartado Postal 70-186, Cd. Mx. 04510, México

\*faustob@ciop.unlp.edu.ar

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*ABSTRACT: In transient thin plasmas assumed in LTE condition such as LIP, the slope of the Boltzmann plot varies with time depending on the experimental conditions in which the plasma was generated. The variation in time of the Boltzmann plot describes a surface in the space defined by the coordinates  $X = \text{Energy}$ ,  $Y = \text{Time}$  and  $Z = \ln(I_j/g_j A_{ji})$ , where  $I_j$  is the integrated intensity of the spectral line,  $g_j$  is the statistical weight of the level  $j$  and  $A_{ji}$  is the transition probability of the considered line, so if we know several points corresponding to that surface it is possible to predict the value of another unknown point. The aim of this work is to represent the time evolution of the intensities of the spectral lines through a reduced number of constants  $B_1, B_2, \dots, B_s$  by means a power series and therefore to know the temporal evolution of the plasma temperature. From the comparison between the polynomials corresponding to different spectral lines which belong to the same ion under analysis, it is possible to determine whether they are useful for Boltzmann plots by a simpler procedure than others, and if their superior energy levels have been properly assigned.*

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## Chemical state determination by WDXRF analysis for geochemical investigations

Victor Chubarov

Vinogradov Institute of Geochemistry, Siberian Branch of Russian Academy of Sciences,  
1A Favorsky st., Irkutsk, Russian Federation

master-17@rambler.ru

**ABSTRACT:** The wavelength-dispersive X-ray fluorescence method is widely used for elemental composition determination in analyzing geological objects, such as minerals, rocks and ores. The position of peak, shape and intensity of some emission lines and satellites are affected by the chemical bond. It allows using X-ray fluorescence also for estimation of determination of valence state and speciation of elements presented in rocks and ores in different chemical states ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ ,  $\text{S}^{2-}$ ,  $\text{S}^{4+}$  and  $\text{S}^{6+}$ ). We investigated influence of chemical bond on intensity of X-ray fluorescence emission spectra and have developed the number of techniques for determination some elements valence state and speciation in geological objects. Our technique is based on the search of spectrum positions wherein intensity is highly affected by chemical state of elements. Due to intensity of all spectral lines depends on total content of element, we used ratio of chosen lines intensity to intensity of line, in lowest rate affected by chemical state. For iron valence state determination in rocks we used ratio of  $\text{FeK}\beta_5$  line, caused by transition from valence level ( $M_4M_5$ ), to intensity of  $\text{FeK}\beta_{1,3}$  line as the analytical parameter. Those investigations are important in geological, geochemical and petrologic studies, for example to identify oxygen activity in magma and equilibrium between minerals and silicate melts. Precision of  $\text{Fe}^{2+}$  content determination in igneous and sedimentary rocks by our technique was comparable with precision of titrimetric technique, that is more labor-consuming and long than our X-ray fluorescence technique and does not allow analyzing of some object with high manganese contents, such as ferromanganese nodules. Our X-ray fluorescence technique allows to determine not only  $\text{Fe}^{2+}$  content in nodules, but also to estimate  $\text{Mn}^{4+}$  content using ratio of line intensities  $\text{MnK}\beta_5$  and  $\text{MnK}\beta_{1,3}$  as the analytical parameter. Satellites of emission  $\text{K}\beta$  spectrum ( $\text{K}\beta'$ ,  $\text{K}\beta''$ ,  $\text{K}\beta^x$ ) caused by transition from valence levels can be used for estimation of speciation (oxides, silicates or carbonates) of iron and manganese in ores. Those data can be used for estimation of ores quality and further mining. Another element that can be used for ores quality estimation is sulphur. Using ratio of  $\text{SK}\beta'$  satellite and  $\text{SK}\beta_{1,3}$  line intensities ratio allows us to distinguish sulphide sulphur from sulphate and sulphite sulphur, due to  $\text{SK}\beta'$  satellite preconditioned by transition from molecular orbital formed by oxygen. Chemical shifts of  $\text{SK}\beta_{1,3}$  and  $\text{SK}\alpha_{1,2}$  lines allow to determine sulphide sulphur content with precision compared with gravimetric technique. Measurements were performed using equipment of the joint use centers (Geodynamics and Geochronology Center, Isotope-geochemical Research Center) and financially supported by the Russian Foundation for Basic Research (project № 15-05-06709).

## WDXRF analysis of chromium ores

Victor Chubarov\*, Alena Amosova

Vinogradov Institute of Geochemistry, Siberian Branch of Russian Academy of Sciences,  
1A Favorsky st., Irkutsk, Russian Federation

\*master-17@rambler.ru

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**ABSTRACT:** The technique of main components quantitative determination ( $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$  and  $V$ ) in chromium ores by wavelength-dispersive X-ray fluorescence analysis is proposed. We used fusion technique for the homogenization of powder samples. Samples were calcinated in muffle furnace at 950 °C. 180 mg of calcined samples were mixed with 3.6 g of flux and fused in carbon crucibles in high frequency furnace at 1100 °C during 8 minutes. To avoid reduction of  $\text{Cr}^{3+}$  to  $\text{Cr}^{2+}$  and to oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  6 drops of 10%  $\text{KNO}_3$  solution were added. Dilution factor was 1:20. We studied utilization of different fluxes (lithium metaborate, lithium tetraborate and their mix) and concluded that lithium tetraborate provides the best repeatability of measurement and preparation. The measurements of X-ray emission spectra were carried out using a wavelength-dispersive X-ray fluorescence spectrometer S8 Tiger (Bruker, Germany) equipped with the Rh anode X-ray tube and Soller optical system. To correct matrix effects we applied the algorithm of fundamental parameters provided in spectrometer software SpectraPlus. Fifteen calibration samples were analyzed by spectrophotometric, flame photometric and gravimetric techniques and then were used for calibration curves constructions. Mineral composition of analyzed samples varies from igneous rocks of ultrabasic compositions (dunites, serpentinites et al.) with low chromium content (less than 1 %) to chromium ores containing basically minerals chromite  $\text{FeCr}_2\text{O}_4$  and magnesiochromite  $\text{MgCr}_2\text{O}_4$ . Calibration curves for chromium content determination were constructed for two ranges (less than 20 % and 20-40 % mass of chromium). Relative standard deviation for  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{CaO}$  determination was less than 2 rel. %, for  $\text{TiO}_2$ ,  $\text{MnO}$  and  $V$  - less then 8 rel. %. Three certified reference materials of chromium ores were analyzed by proposed X-ray fluorescence technique. Results of analysis and certified values are in good agreement. Proposed technique can be applied for quantitative determination of major components in chromium ores by X-ray fluorescence analysis. Measurements are carried out using equipment of the joint use centers (Geodynamics and Geochronology Center and Isotope-geochemical Research Center).

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## Application of High-Resolution Continuum Source Molecular Absorption Spectrometry with Solid and Solution Sampling for the Determination of Fluorine in Tea Varieties and Their Infusions

Sesil Cizmeci<sup>A</sup>, Nil Ozbek<sup>A</sup>, Hande Tinas<sup>A</sup> and Suleyman Akman<sup>A</sup>

<sup>A</sup>Department of Chemistry, Istanbul Technical University, Maslak, Istanbul, Turkey.

cizmecis@itu.edu.tr

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**ABSTRACT:** Due to detrimental effects of excessive fluorine on human health, its concentration in tea is known as the richest F source is of importance. The tea consumption spread in a wide range from person to person. Some people are heavy addicts and consumes great amounts of tea daily. Therefore, fluorine intake from tea may reach to dangerous levels. In this study, the fluorine concentrations in various black tea, green tea, white tea and other herbal tea samples as well as in their infusions were determined by high resolution continuum source molecular absorption spectrometry applying direct solidsampling and solution techniques, respectively. Total fluorine has been determined in tea samples after digestion by high resolution continuum source MAS. In addition, fluoride ions in tea infusions were determined by ion selective electrode. However, it has not been determined by solid sampling technique. For this purpose, CaF was formed upon addition of calcium to solid samples or infusions in the graphite furnace. Total fluorine concentrations in tea samples and in their infusions were determined via molecular absorption of CaF at 660.440nm applying a pyrolysis temperature of 1000 °C and a molecule forming temperature of 2200 °C for both solid sampling and solution techniques. Solid sampling eliminated the time and reagent consuming digestion and prevent the the loss of analyte which is an important risk for F. The limit of detection and characteristic mass of the method were 0.20 ng and 0.17 ng of fluorine, respectively. It was found that after infusion, the most of the fluorine (>50%) in solid samples were extracted to water depending on the sample and the duration of infusion. Black and green tea samples contained the highest fluorine concentrations.

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## Characterization of ancient colored paintings on the lime-plaster from the 'Teatro Marittimo' of Roman Hadrian's Villa (Rome, Italy)

S. Columbu<sup>A\*</sup>, M. Lezzerini<sup>B,C</sup>, S. Pagnotta<sup>B,C</sup>, S. Raneri<sup>C</sup>, S. Legnaioli<sup>B</sup>, V. Palleschi<sup>B</sup>

<sup>A</sup>Department of Chemical and Geological Sciences, University of Cagliari, Via Trentino, 51 – 09127 Cagliari, Italy

<sup>B</sup>Applied and Laser Spectroscopy Laboratory, Institute of Chemistry of Organometallic Compounds, Research Area of National Research Council, Via G. Moruzzi, 1 – 56124 Pisa, Italy

<sup>C</sup>Department of Earth Sciences, University of Pisa, Via Santa Maria, 53 – 56126 Pisa, Italy

\* [columbus@unica.it](mailto:columbus@unica.it)

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**ABSTRACT:** The research aims to study some rare original coloured painting samples (still present) from the 'Teatro Marittimo' at Villa Adriana (Tivoli territory, Rome). The Villa was designed by the Emperor Hadrian in the years between 118 A.D. and 135 A.D. and belongs to the Cultural Heritage of UNESCO since 1999. The structure of the theatre is characterized by a circular body with an axial entrance that leads into the circular portico supported by Ionic columns topped by a barrel vault. A circular channel delimits an artificial central island in which there are a domus, a secondary residence in the Imperial Villa. The main objective of the research is the study of the original coloured-painting finds, applied on the mortar substrate substantially lime-based that coat the internal walls of the circular perimeter of the 'Teatro Marittimo' using the LIBS and Micro-Raman techniques. LIBS is an already tested laser spectroscopy technique that lends itself well to be used for measurements in a sensitive sector such as the Cultural Heritage. In fact, it is a fast technique (only a few seconds are required for the acquisition of a spectrum) and, especially, minimally destructive (the crater produced by the laser beam is generally of the order of a few microns). The Micro-Raman technique, widely used in the application related to the Cultural Heritage, is known to be non-destructive and very used in molecular recognition of pigments and binders. The analysis allowed a detailed mapping of the chemical composition and identification of pigment, eventually the binders, of the coloured surfaces and to hypothesize the raw materials used in the mixtures. Moreover, through physical, petrographic (OM), XRD, SEM and thermo-gravimetric (TG-DSC) analysis, it was possible to identify: i) the composition of the mortar binder; ii) the physical features of the mortar aggregate (i.e. porosity, density, particle size); iii) the microstratigraphy of samples from the adhesion-surface of the mortar substrate to the bricks of the wall, to the overlapping colour levels of the original painting.

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## Solid Sampling Determination of Pb and Cd in Black Tea Leaf by High Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry

Gabriella Dravecz<sup>\*A</sup>, Nikoletta Laczai<sup>A</sup>, Zsolt Ajtony<sup>B</sup>, László Bencs<sup>A</sup>

<sup>A</sup> Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest, Hungary

<sup>B</sup> Department of Food Science, Széchenyi István University, H-9200 Mosonmagyaróvár, Lucsony utca 15-17, Hungary

\*dravecz.gabriella@wigner.mta.hu

Black tea is one of the most popular non-alcoholic beverages in the world. Besides the essential components, toxic elements can also be detected not only in the tea infusion, but in the dried leaves as well. Lead is one of the most commonly occurring contaminant in the environment, while the source of cadmium is the phosphate fertilizer treated soil [1]. According to WHO, the allowable limit of Pb is 5 mg/kg for food and beverages in Europe, while the provisional tolerable monthly intake for Cd is 25 µg/kg body weight. Determination of Cd in tea leaves and beverages is limited by its presence at trace amounts, which is generally below the detection limits of several solution based instrumental analytical techniques [2]. Direct analyses of solid samples without any sample preparation has several advantages over solution introduction based methods, because it is less time-consuming, since only a minimum of sample preparation is required, more sensitive, since the trace-element content of the sample is not diluted during sample preparation and the risk of their loss and contamination of the sample is reduced to a minimum. Direct solid sampling determination of Cd and Pb in black tea leaf was developed by using high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS-GFAAS). The vaporization/atomization processes were investigated in a transversally heated graphite atomizer by evaporating solid samples of black tea. The best results were obtained by using the Pb I 283.306 nm secondary (relative sensitivity: 42%) and Cd I 228.8018 nm primary analytical lines. The optimal pyrolysis and atomization temperatures were 800 and 1700 °C for Pb while 600 and 2000 °C for Cd. For obtaining the optimal atomization transient for Pb, a mixture of 15 µl HNO<sub>3</sub> (6.5% v/v) and 15 µl NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (1% m/m) modifier was added to each sample just before the analysis. Calibration was performed with the method of standard addition. Correlation coefficients (R values) of the calibrations were 0.9968 for Pb and 0.9735 for Cd. The calibration was linear up to 6 mg/kg for Pb and 0.03 mg/kg for Cd. The Pb and Cd content of tea leaves was 3.67 ± 0.17 mg/kg and 0.026 ± 0.002 mg/kg, respectively. [1] Cupit, M., Larsson, O., de Meeus, C., Eduljee, G. H., & Hutton, M.: Assessment and management of risks arising from exposure to cadmium in fertilizers-II. The Science of the Total Environment, 291 (2002) 189–206. [2] Tanmoy Karak, R.M. Bhagat: Trace elements in tea leaves, made tea and tea infusion: A review, Food Research International 43 (2010) 2234–2252.

## Results of the ChemCam Instrument on Board the MSL-Curiosity Rover: Calibration and geochemistry from minor and traces elements.

Olivier Forni<sup>\*A</sup>, Jens Frydenvang<sup>B</sup>, A. Cousin<sup>A</sup>, O. Gasnault<sup>A</sup>, S. Maurice<sup>A</sup>, P.-Y. Meslin<sup>A</sup>, A. Ollila<sup>B</sup>, V. Payré<sup>C</sup>, R.C. Wiens<sup>B</sup>, The ChemCam Team.

<sup>A</sup>Institut de Recherche en Astrophysique et Planétologie, University of Toulouse, CNRS, 9, av. du colonel Roche Toulouse, France; <sup>B</sup>Los Alamos National Laboratory, ISR-2, Los Alamos, USA; <sup>C</sup>GéoRessources, Nancy, France

\*olivier.forni@irap.omp.eu

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*ABSTRACT: The ChemCam LIBS instrument on board the MSL-Curiosity rover has acquired more than 400000 spectra of the surface of Mars during its five years of operation. ChemCam is able to detect the major elements present in rocks as well as some key minor and trace elements. An extended team effort resulted in a new multivariate calibration of the major elements thanks to an extended database which has also been used for new calibration curves for some of the minor elements identified by ChemCam. Among the trace elements, boron was recently detected, the presence of which can place constraints on the thermodynamics of fluids that circulated near the surface of Mars. Groundwater was omnipresent on Mars and is responsible for the formation of veins and concretions of various types. Among them, many observations of light-toned veins dominated by calcium-sulphates indicate the presence of fluorine detected through its CaF LIBS molecular emission, chlorine associated with sodium, phosphorus associated in recent observations with magnesium, and high levels of manganese associated with high contents of iron. Recent observations in mud cracks has also revealed some interesting chemical properties with particularly high potassium, perhaps associated with Sulphur. Along the way, ChemCam also analyzed some iron-meteorites in which we detected nickel and phosphorus.*

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## Quantitative major element calibration of the ChemCam instrument on the NASA Mars Science Laboratory Curiosity rover

Jens Frydenvang<sup>\*A</sup>, Olivier Forni<sup>B</sup>, Samuel M. Clegg<sup>C</sup>, Ryan B. Anderson<sup>D</sup>, Roger C. Wiens<sup>C</sup>, Agnes Cousin<sup>B</sup>, Sylvestre Maurice<sup>B</sup>, Olivier Gasnault<sup>B</sup> and the ChemCam Team

<sup>A</sup>Natural History Museum of Denmark, University of Copenhagen, Copenhagen, Denmark;

<sup>B</sup>Institut de Recherche en Astrophysique et Planétologie, University of Toulouse, CNRS, Toulouse, France.

<sup>C</sup>Los Alamos National Laboratory, ISR-2, Los Alamos, New Mexico, USA

<sup>D</sup>United States Geological Survey, Flagstaff, Arizona, USA

\*jfrydenvang@snm.ku.dk

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**ABSTRACT:** The NASA Mars Science Laboratory (MSL) Curiosity rover landed in Gale Crater, Mars, in August 2012 to investigate past and present habitability of Mars. To help fulfil this mission, the mast-mounted ChemCam instrument was included in the science payload. ChemCam is the first Laser-Induced Breakdown Spectroscopy instrument operating on another planet and provides the MSL science team the ability to perform measurements of target composition at stand-off distances between 2-7 m from the rover. Since landing, the ChemCam instrument has obtained more than 400,000 spectra from a wide range of targets, covering e.g. rocks, calcium-sulphate veins, soils and even iron-meteorites. As all ChemCam observations are made publically available, this dataset represents perhaps the most comprehensive publically available library of LIBS spectra. Here, the ongoing effort by the ChemCam instrument team to improve the major element quantitative calibration of the LIBS measurements will be presented, including details on the major-element quantitative calibration currently utilized by the ChemCam instrument. This calibration utilizes two separate multivariate data analysis methods, Independent Component Analysis regression and Partial Least Squares regression; and takes advantage of the continuous effort to expand the ChemCam calibration dataset acquired using the ChemCam replica instrument located at the Los Alamos National Laboratory, USA.

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## Construction and initial characterization of a spatially heterodyne LIBS spectrometer

Dávid J. Palásti <sup>A</sup>, István Rigó <sup>B</sup>, Miklós Veres <sup>B</sup>, Gábor Galbács <sup>A\*</sup>

<sup>A</sup> Department of Inorganic and Analytical Chemistry, University of Szeged, Hungary;

<sup>B</sup> Department of Applied and Nonlinear Optics, Wigner Research Centre for Physics, Budapest, Hungary.

\*galbx@chem.u-szeged.hu

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**ABSTRACT:** The spatial heterodyne (SH) detection concept was originally developed and proposed for use in interstellar spectroscopy for the detection of weak spectral features by Harlander et al [1]. The SH optical setup is similar to that of the Michelson interferometer, with the mirrors replaced by diffraction gratings positioned at fixed, equal distances from the beamsplitter and are slightly tilted. The tilt is required to provide back-diffraction for wavelengths within the spectral range covered. The gratings need to be precisely aligned so that their grooves are parallel and their tilting angle is the same. The resulting interference pattern is recorded by a CMOS or CCD camera and the spectrum is recovered by using Fourier transformation [2]. SH spectrometers have two major advantages over the commonly used dispersive spectrometers. Their higher light throughput provides them with a significantly higher sensitivity and their estimated resolving power can be twice as high as in grating spectrometers. The construction is also compact, contains no moving parts and can be realized with moderately priced optical components. SH spectrometers have a great potential in analytical spectroscopy. The predicted benefits were already realized in branches of spectroscopy studies working with (quasi) cw light sources, such as astronomical emission, IR and Raman spectroscopies. In 2014, Gornushkin et al. reported about the first, and so far the only one, successful implementation of SH-LIBS spectroscopy [3]. The goal of the present work is to construct a compact SH-LIBS spectrometer fit for routine analytical use. This ongoing construction work involves the optimization of the optical setup, the selection of appropriate gratings, the development of efficient data evaluation algorithms for the processing of the interferograms, the development of practical spectral scanning and wavelength calibration features, etc. The spectral detection also needs to be synchronized with the ablative laser pulse with microsecond time resolution, which requires a tight control of the sensitivity and triggering capabilities of the camera used. Our contribution will provide preliminary performance data on our SH-LIBS system. [1] J. Harlander, R. J. Reynolds, F. L. Roesler, *Astrophys. J.* 396 (1992) 730. [2] M. Lenzner, J.-C. Diels, *Opt. Express* 24 (2016) 253838. [3] I. B. Gornushkin, B. W. Smith, U. Panne, N. Omenetto, *Appl. Spectrosc.* 68 (2014) 1076.

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## Investigation of apatite grains in amphibolite rock samples by laser and X-ray spectroscopy methods

Patrick Janovszky <sup>A</sup>, Félix Schubert <sup>B</sup>, Tivadar M.-Tóth <sup>B</sup>, Gábor Galbács <sup>A\*</sup>

<sup>A</sup> Department of Inorganic and Analytical Chemistry, University of Szeged, Hungary;

<sup>B</sup> Department of Mineralogy, Geochemistry and Petrology, University of Szeged, Hungary.

\*galbx@chem.u-szeged.hu

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**ABSTRACT:** The pre-Mesozoic basement of the Pannonian Basin (PB) can be viewed as a mosaic of unrelated crystalline blocks. Drillcore investigations show that they are mainly composed of medium- and high-grade polymetamorphic rocks with a broad spectrum of minerals. The dominant rock-forming minerals of these metamorphics are different kinds of silicates but other constituents of subordinate quantity (so-called accessory minerals) may serve enormous information about the origin, formation conditions, age, etc. of the host rock. One of the most frequent of these is apatite ( $(\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH}))$ ) that often incorporates a significant amount of rare earth elements (REE) and some trace elements in its crystal lattice in the structural position of  $\text{Ca}^{2+}$ .

The object of this study is an amphibolite rock sample of the PB, which contains apatite grains in significant fraction and size (up to 400  $\mu\text{m}$ ). Both under polarized light and UV excitation (360-370 nm) as well as on SEM-cathode luminescent images, these apatite grains often show heterogeneous, patchy appearance. Some of the apatite grains contain uniformly oriented trails of tiny fluid inclusions along healed microfractures. The main goal of this research was to study the chemical composition of the apatite grains by various spectroscopy methods with high spatial resolution and laser or X-ray excitation (e.g. LIBS, LA-ICP-MS,  $\mu\text{XRF}$ , Raman microscopy, LIF, etc.) in order to find explanation to their different appearance (i.e. patchy or clear). The relation of trace elemental content and optical inhomogeneities of the grains could provide insights into the formation conditions of these accessory grains and the late, brittle evolution of the study area.

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## Direct determination of silicon in oil-in-water emulsions by high-resolution continuum source flame atomic absorption spectrometry

Beatriz Gómez-Nieto<sup>A</sup>, M<sup>a</sup> Jesús Gismera<sup>\*A</sup>, M<sup>a</sup> Teresa Sevilla<sup>A</sup>, Susana Cofrades<sup>B</sup>, Jesús R. Procopio<sup>A</sup>

<sup>A</sup> Departamento de Química Analítica y Análisis Instrumental. Facultad de Ciencias. Universidad Autónoma de Madrid, C/. Francisco Tomas y Valiente 7, 28049 Madrid, Spain. <sup>B</sup> Instituto de Ciencia y Tecnología de Alimentos y Nutrición, C/José Antonio Novais, 10, 28040 Madrid, Spain.

\*mariajesus.gismera@uam.es

**ABSTRACT:** Silicon is not considered nowadays as an essential element for humans, but it is suspected that this metalloid plays a key role in the development of bones, cartilage and other connective tissues. In addition, recent findings provide that silicon may have a modulating effect on the immune and inflammatory response, and has been associated with mental health. Due to these benefits, silicon is used in cosmetic and pharmaceutical products and to prepare functional foods. Silicon incorporation in these products is often performed in emulsions or double emulsions. Oil-in-water multiple emulsions are complex liquid dispersions employed to entrap, protect and control the release of different substances such as minerals. The development and implementation of analytical methodologies that allow the accurate and precise quantification of silicon is of great interest for laboratories devoted to routine analysis. However, silicon determination is considered to be one of the most challenging tasks in elemental analysis. This is partially due to the high risk of sample contamination owing to the ubiquity of this element and the possible loss of this analyte during the sample pretreatment process owing to the high volatility of some silicon compounds. In this context, the development of analytical methodologies based on direct analysis of the sample are considered very interesting approaches to determine silicon compared to traditional methods based on wet digestion of the samples. As additional benefits, these analytical strategies are simple and increase the speed of analysis. High-resolution continuum source atomic absorption spectrometry with flame atomizer (HR-CS FAAS) improves the possibilities for the development of direct methods. HR-CS FAAS allows the detection and correction of spectral interferences from the matrix sample as well as carry out an automatically and truly simultaneous background correction for continuous events which leads to more stable baselines. Moreover, due to the high resolution (a few picometers per pixel) provided by HR-CS FAAS instrument, it is possible to separate the absorption signal of silicon at 251.611 from the one at 251.432 nm that is typically a problem using traditional AAS. This work presents the development of a fast and straightforward method based on HR-CS FAAS for the determination of silicon in different oil-in-water emulsions. To achieve this purpose, the main analytical line of silicon at 251.612 nm was select, and the burner height and flame composition were optimized. The feasibility to perform the calibration with aqueous standards was evaluated and the principal analytical parameters were calculated. Finally, the proposed analytical approach was applied to determine this metalloid in different oil-in-water emulsions.

## Method development for the determination of iAs in rice using hydride generation atomic absorption spectrometry (HG-AAS)

Hajnalka Fige<sup>A</sup>, Sándor Harangi\*<sup>A</sup>, Maud Costedoat<sup>B</sup>, Jean-Pierre Lener<sup>B</sup>, Edina Baranyai<sup>A</sup>

<sup>A</sup>Agilent Atomic Spectroscopy Partner Laboratory, Department of Inorganic and Analytical Chemistry, University of Debrecen, H-4032 Debrecen, Hungary.

<sup>B</sup>Agilent Technologies, 91978 Les Ulis, France.

\*harangi.sandor@science.unideb.hu

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**ABSTRACT:** Some plants can easily accumulate arsenic from the environment originating of natural and/or anthropogenic sources. These compounds can be harmful for the human health. Rice is important in the catering of population; it is the most widely consumed staple food for approximately 3.5 billion people. Arsenic is therefore a major concern if present in rice or rice based food products. Commission Regulation (EC) No 2015/1006 amending regulation No 1881/2006 sets maximum levels for arsenic in rice and rice based products from 0.1 to 0.3 mg Kg<sup>-1</sup> that applies from 1 January 2016. The aim of this study is to develop a cost-effective, highly sensitive analytical method to determine and control the level of inorganic arsenic in rice in accordance with European Regulation. The HG-FAAS technique is the most practical among the atomic spectrometry methods if one element is to be measured. For the application development, rice CRM material was used and prepared by microwave digestion with the mixture of concentrated acids. iAs was measured in several digested commercially available rice products following the developed method. Acknowledgement: The research was supported by the EU and co-financed by the European Regional Development Fund under the project GINOP-2.3.2-15-2016-00008. We would like to highly acknowledge Agilent Technologies (Novo-Lab Ltd.) for providing 240FS AA and VGA 77 instrument for the elemental analysis.

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## Analyzing Carbonate Muds by Handheld LIBS.

Eugene C. Rankey<sup>\*A</sup>, Richard R. Hark<sup>B</sup>, Chandra S. Throckmorton<sup>C</sup>, Russell S. Harmon<sup>D</sup>, Andrew M. Somers<sup>E</sup>, Kaitlin E. Bompiani<sup>B</sup>, and Leslie M. Collins<sup>C</sup>

<sup>A</sup>KICC, Department of Geology, University of Kansas, Lawrence, KS 66045, USA

<sup>B</sup>Department of Chemistry, Juniata College, Huntingdon, PA 16652, USA

<sup>C</sup>Department of Electrical and Computer Engineering, Duke University, Durham, NC 27708, USA

<sup>D</sup>Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC 27695, USA

<sup>E</sup>SciAps, Inc., 2 Constitution Way, Woburn, MA 01801, USA

\*grankey@ku.edu

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**ABSTRACT:** Despite being mineralogically 'simple,' consisting of only two or three minerals, elemental variations in carbonate sediment can provide important insights into chemical and biological oceanographic processes. We have analyzed modern carbonate sediments to explore the use of a handheld LIBS system for assessing geochemistry of, and controls on, marine carbonate sedimentary systems. These muds were sampled in shallow (< 11 m) water depths from six locations worldwide - Alacran Reef (Mexico); Yucatan Shelf (Mexico); Crooked-Acklins Platform (Bahamas); Caicos Platform (Turks and Caicos Islands); Maupiti Atoll (French Polynesia); and Nonouti Atoll (Republic of Kiribati). The SciAps Z500 LIBS analyser used for this study demonstrates that handheld LIBS can be an effective tool for the rapid analysis of geological materials in the field, without the need for sample preparation, and LIBS analysis can be used in conjunction with multivariate statistical processing for geomaterial discrimination and provenance determination. This handheld LIBS system is well suited to geochemical applications, particularly real-time analysis in the field, due to its portability, broad spectral range from 180 to 675 nm, argon purging, translational stage for 3-D beam rastering, and built-in camera for targeting and documentation of analysis. Carbonate muds were pressed into 40 mm pellets without any binding material. For each location in an 11-point grid 5 laser pulses were collected and randomly averaged in groups of 5 to produce at least 10 spectra. Principal Component Analysis was used to condense the full spectrum data into a meaningful representation of several combined features and then Partial Least Squares Discriminant Analysis was used for the classification analysis. The LIBS results reveal subtle difference in composition among the six depositional carbonate areas, with Sr, Ca, and (to a lesser extent) Mg the main compositional components contributing to the distinctions. Overall, classification success for the carbonate mud suite was 96%. About 5% of the Yucatan spectra were confused with those from the Nonouti Atoll and just under 10% of Caicos Platform spectra were confused with those from the Crooked-Acklins Platform and vice-versa at a level just over 5%. This result documents differences in the bulk composition of carbonate muds in their depositional environment, attesting to different mineralogy and proportions of biotic and abiotic components, with spectral loadings from the LIBS analysis documenting, as might be expected, that the main compositional components contributing to the discrimination in are, Sr, Ca, and Mg to a lesser extent. Interestingly, the 288.16 nm line for Si was more prominent in LIBS spectra for the Yucatan Shelf mud, identifying a biosilicious component that is mostly absent in the mud from the other locations. At a larger spatial scale, the six carbonate mud localities group well by ocean basin (Pacific, Gulf of Mexico, and Atlantic), with 320 out of 330 (98.9%) spectra correctly classified. The similarities among regions implies that water chemistry, in particular nutrients, salinity and alkalinity, is likely to be influencing the composition of accumulated carbonate at both the local and the regional spatial scales. For example, the Yucatan is impacted by upwelling water, favoring biosilicious organisms and more calcite-dominant fauna. By contrast, Caicos and the Bahamas are regions of elevated alkalinity and vigorous tides, factors which favor the production of non-skeletal (and aragonitic) sediment.

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## Analysis of aerosols via calibration-free laser-induced breakdown spectroscopy in helium.

Mohamed Boudhib<sup>A</sup>, Jörg Hermann<sup>\*B</sup>, Christophe Dutouquet<sup>A</sup>

<sup>A</sup>Institut National de l'Environnement Industriel et des Risques, Verneuil-En-Halatte, France;

<sup>B</sup>LP3, CNRS - Aix-Marseille University, Marseille, France

\*hermann@lp3.univ-mrs.fr

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**ABSTRACT:** The detection and characterization of particles in the air and water are major challenges in the field of environmental survey. Recently, particular efforts have been dedicated to the development of in situ real-time measurements of size and composition of particles in gaseous or liquid suspensions [1,2]. Laser-induced breakdown spectroscopy (LIBS) is a promising technique for such type of analyses. However, the variability of particle size and density make the measurement calibration difficult [3]. To overcome this problem, we have developed a calibration-free LIBS measurement procedure. Based on modeling of the laser-induced plasma, the composition of aerosols is deduced by comparing the measured emission spectrum to a spectrum computed for plasma in local thermal equilibrium. To illustrate the feasibility, the breakdown was produced in helium at atmospheric pressure. Due to the high initial temperature and the large thermal conductivity, breakdown in helium leads to rapid aerosol vaporization and a more uniform plasma, compared to breakdown in air or argon. We demonstrate that the plasma can be described by a partial thermodynamic equilibrium. Thus, the population number densities of all plasma species follow the Boltzmann equilibrium distribution, except of helium atomic and ionic number densities. By recording spectra at different delays with respect to the laser pulse, we show that accurate analyses of the aerosol composition are only possible for  $t \leq 1\mu s$ , when the electron density is large enough to ensure the collisional equilibrium for the aerosol species [4]. In agreement with recent LIBS analyses of solid glass and alumina, the present results encourage compositional measurements of aerosols via laser-induced breakdown spectroscopy. [1] D. W. Hahn, M. M. Lunden, Detection and Analysis of Aerosol Particles by Laser-Induced Breakdown Spectroscopy, *Aerosol Sci. Technol.* **33**, 30 (2000). [2] C. B. Faye, T. Amodeo, E. Frejafon, N. Delepine-Gilon, C. Dutouquet, Sampling considerations when analyzing micrometric-sized particles in a liquid jet using laser induced breakdown spectroscopy, *Spectrochim. Acta Part B* **91**, 5 (2014). [3] V. Hohreiter, D. W. Hahn, Plasma-particle interactions in a laser-induced plasma: implications for laser-induced breakdown spectroscopy, *Anal. Chem.* **78**, 1509 (2006). [4] M. Boudhib, J. Hermann, C. Dutouquet, Compositional analysis of aerosols using calibration-free laser-induced breakdown spectroscopy, *Anal. Chem.*, **88**, 4029 (2016).

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## Formation Mechanisms of Calcium Monofluoride in Graphite Furnace Molecular Absorption Spectrometry and Interactions with Competitive Elements

Suleyman Akman<sup>A</sup>, Nil Ozbek<sup>A</sup>

<sup>A</sup> Department of Chemistry, Istanbul Technical University, Maslak, Istanbul, Turkey.

\*akmans@itu.edu.tr

**ABSTRACT:** Fluorine can be determined via molecular absorption of a suitable diatomic metal monofluoride generated in a graphite furnace using a high resolution continuum source atomic absorption spectrometer. Calcium monofluoride (CaF) is an extensively used diatomic molecule for this purpose due to its suitable wavelength, sufficient bond dissociation energy and low enough limit of detection. In this study, at first, the formation mechanisms of CaF in a graphite furnace was examined. To differentiate the condensed phase and gas-phase combination reactions during CaF formation, Ca and F were both mixed as well as separately pipetted in the cavity of a solid sampler platform. It was assumed that when Ca and F were mixed, both gas-phase and condensed phase interactions occurred whereas in the case that Ca and F were separated, they did not contact prior to volatilization and only gas-phase reactions were responsible for the formation of CaF. The main mechanism for the formation of CaF was gas-phase combination reaction between Ca and F because CaF was formed irrespective of whether Ca and F were mixed or separated. The CaF sensitivities for the both cases were not significantly different. Moreover, when a solid tea sample and Ca solution were separately introduced on the platform, a CaF peak with only an insignificant sensitivity loss compared to mixed case was observed as well. Even if very small amounts of the solid salts of F as NaF and Ca as the nitrate were put on the platform separately, a huge CaF was detected. Finally, when calcium was deposited in a graphite tube and then F was introduced using a new calcium-free platform, again CaF signal was detected which is another evidence for the gas-phase combination reaction.

Secondly, the interaction mechanisms of some metals such as gallium, aluminum, barium and strontium on the formation of CaF were searched. For this purpose, (i) "Ca+F+interferent" were mixed on the platform (ii) "Ca+F" were mixed on one side of the platform whereas the interferent was pipetted on the other side (iii) Ca was pipetted on one side of the platform and "interferent+F" were mixed on the other side. In the experiments, 0.05 µg of F and 10 or 20 µg of Ca and different amounts of interferents were used. It was proved that again gas-phase combination interactions between the interferents and fluorine played a dominant role in the interferences because sensitivities for CaF were reduced irrespective of whether the interferents, calcium and fluorine were mixed or separated in different combinations, namely cases (i) –(iii).

Finally, the effects of chloride, bromide, phosphate and sulfate on the determination of F via CaF applying the same strategy were low compared to metals. This was attributed to the high amount of Ca which was more than enough to react with both F and the interferents satisfactorily.

## Collisional Radiative Model for Filamentation of Tightly Focused Femtosecond Laser Pulses in Air.

Alexey Ilyin<sup>\*A,B</sup>, Sergey Golik<sup>A,B</sup>, Konstantin Shmirko<sup>A,B</sup>, Alexander Mayor<sup>A</sup>, Dmitriy Proschenko<sup>B,C</sup>

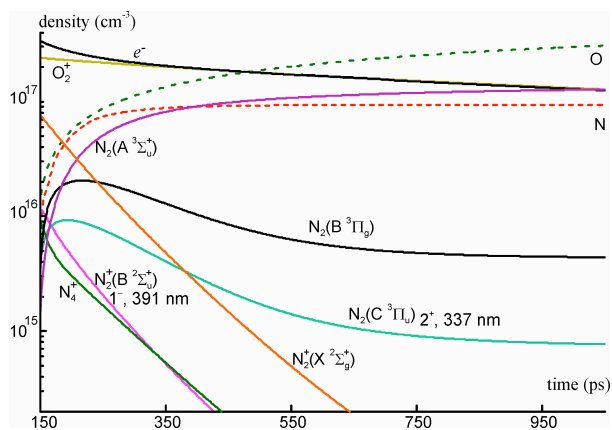
<sup>A</sup>Institute of Automation and Control Processes, FEB RAS, 5, Radio St., Vladivostok, 690041, Russia;

<sup>B</sup>Far Eastern Federal University, 8, Sukhanova St., Vladivostok, 690090, Russia;

<sup>C</sup>Maritime State University, 50a, Verkhneportovaya St., Vladivostok, 690059 Russia.

\*kunashir@gmail.com

**ABSTRACT:** Atomic and molecular emission of the filament plasma generated by femtosecond laser in air was investigated in our previous work [1]. Ti:Sapphire laser radiation (800 nm, 1.1 mJ, 48 fs) was focused by 5 cm focal length lens. Following persistence of emission were detected: 400 ps ( $N_2^+$  391.2 nm), 1 ns ( $N_2$  337 nm) and 150 ns ( $N$  I 746.8 nm,  $O$  I 777.4 nm). Here we simulate particle dynamics and make comparison of experimental results and computations. Model includes density dynamics of  $N_2(X, A, B, C)$ ,  $N_2^+(X, B)$ ,  $N_4^+$ ,  $O_2^+$ ,  $N$ ,  $O$ , electrons. We account for emission; molecule dissociation; electron impact ionization and excitation; three-body and dissociative recombination; heavy particles and electron quenching, Joule heating by post-pulses and amplified spontaneous emission from regenerative amplifier. Temporal evolution of plasma species densities is shown below. This study was supported by the Russian Science Foundation (project no. 14-50-00034).



1. Alexey A. Ilyin, Sergey S. Golik, Konstantin A. Shmirko, Absorption and emission characteristics of femtosecond laser plasma filaments in the air // *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2015, Vol. 112, pp. 16–22

## Comparison of theoretical and experimental studies of methane adsorption on PdO/Al<sub>2</sub>O<sub>3</sub> structured catalyst

P. Jodłowski<sup>\*A</sup>, I. Czekaj<sup>A</sup>, R. J. Jędrzejczyk<sup>B</sup>, D. Chlebda<sup>C</sup>

<sup>A</sup>Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Kraków, Poland; <sup>B</sup>Malopolska Centre of Biotechnology, Gronostajowa 7A, 30-387 Kraków, Poland; <sup>C</sup>Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Kraków, Poland

\*jodlowski@chemia.pk.edu.pl

**ABSTRACT:** Although the activation of methane molecule has long been studied for various processes and a huge amount of information in this topic can be found in the literature it remains an unsolved problem with a lot of controversies. In the literature, the general agreement is that the initial step in methane catalytic combustion is the hydrogen removal with the formation of methyl radical. However, the methane molecule is considered to be the most resistant to be oxidized due to its high symmetry. The mechanism of the C-H activation includes two possible pathways running either on metal or metal oxide catalysts. The first mechanism distinguishes the heterolytic splitting of C-H resulting in the formation of methyl radical. The second mechanism assumes the homolytic splitting of C-H bond by oxygen active species. However, the mechanism puts forward both acidic and basic surface active sites to be very important in methane activation. The mechanism becomes more complicated, under the rich oxygen conditions for biogas engines and turbines which is considered in the presented study. Here, we deal with the theoretical and experimental studies on mechanism of methane catalytic combustion over PdO/Al<sub>2</sub>O<sub>3</sub> structured catalyst. The aim of this research was to correlate the information obtained from the DFT calculations with the experimental in situ DRIFT and UV-Vis experimental results. The series of palladium/alumina structured catalysts were obtained using combined sol-gel method and deposition on FeCr alloy structured reactors. The obtained catalysts were examined by XRF and in situ techniques such as:  $\mu$ Raman, DRIFT and UV-Vis. Ab initio calculations within the density functional theory are used implemented into StoBe software. The exchange and correlation functional is approximated with a scalar relativistic spin paired Perdew-Burke-Ernzerhof (PBE) formula. Several clusters, which represent Al<sub>2</sub>O<sub>3</sub> (100), have been analyzed and finally the Al<sub>30</sub>O<sub>74</sub>H<sub>58</sub> cluster has been used in CH<sub>4</sub> adsorption studies. Several configurations, electronic structure (charges, bond orders) and density of states have been analyzed to determine feasible pathways for the oxidation process. The methane oxidation cycles have been considered as a further step at differently oxidized Pd nanoparticles: i) at oxygen deficient conditions, ii) at oxygen rich conditions. The comparison of the theoretical and experimental studies allowed to propose mechanisms of methane combustion under rich and lean reaction conditions.

## Laser Induced Breakdown Spectroscopy for Soil Specific Surface Area Estimation

Maria Knadel<sup>A\*</sup>, Cecilie Hermansen<sup>A</sup>, Per Moldrup<sup>B</sup>, Mogens H. Greve<sup>A</sup>, Emmanuel Arthur<sup>A</sup> and Lis W. de Jonge<sup>A</sup>

<sup>A</sup>Aarhus University, Department of Agroecology, Blichers Allé, DK-8830 Tjele, Denmark

<sup>B</sup>Aalborg University, Civil Engineering, Thomas Manns Vej 23, DK-9200 Aalborg East, Denmark

\*maria.knadel@agro.au.dk

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**ABSTRACT:** The soil specific surface area (SA) ( $\text{m}^2/\text{g}$ ) is a property of the solids defined as the total surface area per unit mass of soil. Due to the effects of SA on soil physical and chemical properties, it is important for processes such as water retention and movement, contaminant adsorption, microbial attachment and nutrient dynamics in soils. However, the conventional analyses for SA determination are tedious and for some methods, hazardous chemicals are involved. Laser induced breakdown spectroscopy (LIBS) is a rapid technique with potential for analysis of elements present in the soil. Recently, LIBS was successfully used to estimate several soil properties, including clay content. We hypothesise that since SA is linked to the clay mineralogy and particle size distribution of soils, the SA can be estimated accurately using LIBS. The aims of this study were: i) to test the feasibility of using LIBS for SA determination, ii) to compare the predictive ability of the LIBS model for predicting SA with that for predicting clay, and iii) to test if additional variables selection improves the predictive ability of the calibration models. The investigated samples, comprising 115 Danish topsoil samples, were analysed for SA and clay content using the Ethylene Glycol Monoethyl Ether (EGME) and the hydrometer methods, respectively (SA:  $2.98\text{--}125.71 \text{ m}^2\text{g}^{-1}$  and clay:  $0.03\text{--}0.46 \text{ kg kg}^{-1}$ ). The LIBS measurements (175–430 nm) were performed using an Nd-YAG laser with an UV diode array spectrometer and a silica fibre optic. The data set was divided into calibration ( $n=86$ ) and validation sets ( $n=29$ ) for SSA and clay modelling separately in order to ensure a full coverage of both SSA and clay range in the calibration data sets. The LIBS spectra were correlated with the SA and clay content using Partial Least Squares (PLS) regression. Interval Partial Least Squares (iPLS) regression was used as a variable selection method for the two soil properties individually. Predictive ability of the models was compared using a ratio of performance to inter-quartile range (RPIQ). Lower predictive ability of PLS models for SA than for clay was obtained. Further variables selection resulted in improved accuracy for both SSA and clay (RPIQ of 2.9 and 3, respectively) in comparison to using the entire LIBS spectrum (RPIQ of 1.9 and 2.3, respectively). Moreover, the application of iPLS decreased the number of variables from 2045 (the entire LIBS spectrum) to 200 and 400 for the determination of SSA and clay, respectively. The results for SSA are promising and need further validation on a larger dataset with more variable clay mineralogy.

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## Thermodynamic and Transport Properties of Plasmas including Silicon-based Compounds

Gianpiero Colonna<sup>A</sup>, Antonio D'Angola<sup>BA</sup>, Lucia Daniela Pietanza<sup>A</sup>, Mario Capitelli<sup>A</sup>, Fernando Pirani<sup>C</sup>, Elena Stevanato<sup>D</sup>, Annarita Laricchiuta<sup>\*A</sup>

<sup>A</sup>PLASMI Lab CNR NANOTEC, Bari, Italy;

<sup>B</sup>Scuola di Ingegneria, Università della Basilicata, Potenza, Italy;

<sup>C</sup>Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Perugia, Italy;

<sup>D</sup>Dept. of Engineering for Innovation, University of Salento, Lecce, Italy.

\*annarita.laricchiuta@cnr.it

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*ABSTRACT: The knowledge of equilibrium composition and transport properties of plasmas represents a fundamental information for the theoretical support to the LIBS technique. In the ablation of rocks and of meteorites it is of particular interest to characterize plasmas containing silicon-based chemical species. Thermodynamics properties and transport coefficients have been derived for SiO<sub>2</sub> and SiC plasmas using EquilTheTA, a web-based tool, characterized by high efficiency and reliability also in extreme simulation conditions. The core databases of physical-chemical properties include the accurate description of species level structure and of the dynamics of binary interactions, studied within either multi-potential or phenomenological approaches.*

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## Calibration strategy for quantitative LIBS measurements in extremely variable plasma conditions, and for reduction of the matrix effect

Violeta Lazic, Antonella De Ninno

ENEA, Dep. FSN-TECFIS-DIM, Via E. Fermi 45, 00044 Frascati (Italy)

\*violeta.lazic@enea.it

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*ABSTRACT: Scope of this work was to study behavior of the line intensities from different species in extremely variable laser induced plasmas, and to establish a calibration approach which could improve the analytical precision also in common LIBS experiments. To this aim we acquired LIBS spectra from particles of certified powder samples, randomly dispersed over a silica wafer covered with a thin film of ultra-pure oil. The LIBS line intensities strongly depend both on the particle weight and distribution inside the laser spot, fluctuating between the detection limit and the detector's saturation level. In presence of such extreme plasma intensity variations a widely diffused spectra averaging method, although coupled with line normalization for two sample's elements, produces errors excessively large for any kind of quantitative measurement. Differently, consideration of the relative slopes, for example by plotting a Ca I line intensity versus a Mg I line intensity, produces well aligned data points. The axis intercept depends on the plasma temperature, here variable, but the slope is directly related to the relative element concentrations in the sample. By considering the slopes of line intensities from two elements it was possible to reduce drastically the relative standard deviation and to obtain the calibration curves for quantitative LIBS measurements. Furthermore, we applied theoretical simulations of the line intensities in order to choose the line pairs less sensitive to variations of the plasma temperature, and this procedure brought to a reduction of the matrix effect because the examined powders tend to fluctuate around very different average plasma temperatures.*

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## Detection of Bacterial Pathogens in Water Using Affinity Aptamers and Inductively Coupled Plasma Mass Spectrometry

Camille Hamula, Feng Li, Yanming Liu, Zhixin Wang, Qiang Zhao, X. Chris Le\*, Xing-Fang Li\*

Analytical and Environmental Toxicology Division, Department of Laboratory Medicine and Pathology, Faculty of Medicine and Dentistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G3

\*xc.le@ualberta.ca

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*ABSTRACT: Escherichia coli O157 contamination of water and food is one of the leading causes of outbreaks of human gastroenteritis worldwide. Protection of water and food safety against bacterial contamination and rapid diagnosis of infectious agents, including E. coli O157:H7, require sensitive, simple and fast assays for detection of bacterial pathogens. We describe here a rapid and sensitive assay for the E. coli O157:H7 bacteria by using antibody affinity binding, gold nanoparticle (AuNP) labeling, and inductively coupled plasma mass spectrometry (ICPMS) detection. Taking advantage of the signal amplification property of AuNPs and the high sensitivity of ICPMS, the assay was able to detect as few as 500 E. coli O157:H7 cells in 1 mL of sample (500 CFU/mL). Tests with non-pathogenic E. coli (DH5a, ATCC35218, and ATCC25922) showed high specificity of the assay for E. coli O157:H7. Each assay was completed within 40 min. To expand the assay for a variety of pathogens, we also developed novel aptamers against specific live bacterial pathogens, for example, live Streptococcus pyogenes. We further demonstrate the potential of aptamer-ICPMS assays for detecting a variety of bacterial pathogens.*

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## Determination of mercury in geothermal fluids employed as sources in power plants.

Alessandro Lenzi<sup>\*A,C</sup>, Antonio Caprai<sup>A</sup>, Alessandro D'Ulivo<sup>B</sup>, Massimo Onor<sup>B</sup>, Marco Mascherpa<sup>B</sup>, Marco Paci<sup>C</sup>, Alessandro Bettini<sup>C</sup>

<sup>A</sup>C.N.R. - Consiglio Nazionale delle Ricerche, Istituto di Geoscienze e Georisorse, Via Giuseppe Moruzzi, 1 - 56124 Pisa (I), <sup>B</sup>C.N.R. - Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti Organometallici, S.S. di Pisa - Via Giuseppe Moruzzi, 1 - 56124 Pisa (I), <sup>C</sup>Enel Green Power, Via Andrea Pisano, 120 - 56122 Pisa (I).

\*alessandro.lenzi@igg.cnr.it

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**ABSTRACT:** Mercury is one of the most important source of pollution in geothermal vapor sources which are employed in power plants. Mercury must be efficiently removed from the vapor during the working cycle of the power plant in order to bring its concentration level below the safety threshold and emission limits in waste vapors/gases. It is important to determine the concentration of mercury in the vapor source,  $Hg_{VS}$ , the concentration of mercury removed,  $Hg_R$ , and the concentration of mercury in the waste gases/vapors,  $Hg_W$ , for a correct monitoring of the mass balance of mercury circulating in the power plant:  $Hg_{VS} = Hg_R + Hg_W$ . The accurate determination of mercury concentration of mercury in the vapor source,  $Hg_{VS}$ , represents the key step for the correct evaluation of the mass balance. The sampling and determination of  $Hg_{VS}$  represents a challenging task both for the difficulties in the sampling step (temperature 200-400°C, pressure 20-40 bars) and by the lack of consolidated methods which guarantee the accuracy of mercury collection and determination. In this work we compared several independent methods with the aim to set-up reliable methods of mercury collection and determination in geothermal fluids: (i) Collection in 1L evacuated glass bottle containing 18mL of 0.25M  $KMnO_4$  in 1.8M  $H_2SO_4$  absorbing solution; (ii) Collection using a modified Gigenbach method: 250 mL evacuated glass flask containing about 80 mL absorbing solution. Three different absorbing solutions were employed: 4M NaOH containing 0.1-0.3 M of permanganate, or persulfate or hypochlorite. Total mercury determination were carried out using both CV-AAS and a direct mercury analyzer (DMA80, Milestone) for sample collected by method (i), and using a direct mercury analyzer (DMA80) for samples collected by method (ii). A good agreement was found among the Hg concentration determined by the different procedures which allows to estimate the concentration of Hg in the geothermal fluids with an uncertainty less than 20%. The use of method (ii) using 0.3M NaClO in 4M NaOH combined with direct mercury determination was found to be an useful alternative to method (i) for its simplicity, the capacity to collect larger volume of geothermal fluid and low blank levels.

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## Measurement of transition probabilities of Mn II lines by laser-induced breakdown spectroscopy.

J. Manrique<sup>\*A</sup>, C. Aragón<sup>B,C</sup>, J. A. Aguilera<sup>B,C</sup>

<sup>A</sup>Facultad de Farmacia, Universidad CEU San Pablo, Urbanización Montepríncipe, Boadilla del Monte, E-28668 Madrid, Spain; <sup>B</sup>Departamento de Física, Universidad Pública de Navarra, Campus de Arrosadía, E-31006 Pamplona, Spain; <sup>C</sup>Institute for Advanced Material (INAMAT), Public University of Navarre, Campus de Arrosadía, E-31006 Pamplona, Spain.

\*jamanros@ceu.es

**ABSTRACT:** Laser-induced breakdown spectroscopy (LIBS) has become a powerful and well-established technique for the measurement of atomic data. In particular, there has been a continuous interest in the determination of accurate values for atomic transition probabilities. These parameters are of interest for atomic structure studies due to their sensitivity to the interaction schemes and, from an applied point of view, because are required to analyse data from astrophysical, fusion and laboratory plasmas. The use of LIBS as a spectroscopic source has a great potential for the measurement of these atomic data since high temperature plasmas from a variety of samples with several ionization stages are easily obtained. Nevertheless, the systematic error caused by the self-absorption of the spectral lines becomes the main difficulty to obtain accurate measurements. In previous works our group has investigated the use of curves of growth and CSigma graphs<sup>1</sup> for the characterization of the plasma and to avoid the systematic errors due to self-absorption. In the present work, this methodology is employed to obtain transition probabilities of ionized manganese. Despite its relevance, accurate values of experimental and theoretical transition probabilities for this ion are scarce<sup>2</sup>. The high energy of the upper levels together with the self-absorption of the stronger transitions involve a challenging experimental difficult for plasma sources whilst theoretical calculations are complex because the energy level structure has an open 3d subshell. The plasmas are generated focusing a Nd:YAG laser onto the surface of fused glass samples with different concentrations of manganese. The parameters that characterize the plasma are obtained from the fitting of the experimental data for well-known reference lines whereas the electron density is obtained by measuring the Stark broadening of the H<sub>α</sub> line. Afterwards, the transition probability values are obtained by fitting the experimental intensities to the Cσ graph. This method allows us to report transition probabilities avoiding self-absorption of several Mn II spectral lines including a wide range of intensities and upper level energies. References: <sup>1</sup> C. Aragón and J. A. Aguilera, JQSRT 149 (2014) 90. <sup>2</sup> E. A. Den Hartog, J. E. Lawler, J.S.Sobeck, C. Sneden and J. J. Cowan, ApJS 194 (2011) 35.

## Thermospecies of mercury in lichens as bioindicators of air pollution

Nikolai Panichev <sup>\*A</sup>, Mpho Mathebula <sup>A</sup>, Khakhathi Mandiwana <sup>A</sup>, Nikolay Mashyanov <sup>B</sup>, Sergei Pogarev <sup>B</sup>

<sup>A</sup> Tshwane University of Technology, Pretoria, Republic of South Africa, <sup>B</sup> St. Petersburg State University, St. Petersburg, Russia

\*panichevn@tut.ac.za

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**ABSTRACT:** For the general assessment of mercury air transport and deposition, the use of lichens is one of the plausible possibilities to perform rapid monitoring of vast terrestrial ecosystems. Results of many investigations show that the mercury level in lichens perfectly reflects average mercury concentration in atmospheric air. However, the pathway of mercury into the lichens is still not clearly understood, because there are several ways for mercury intake and accumulation by lichens: adsorption of gaseous elemental (GEM,  $Hg^0$ ), gaseous oxidized (GOM,  $Hg^{2+}$ ), or particulate bound (PBM) mercury. Taking into account that 95 - 99% of total atmospheric mercury is  $Hg^0$ , it is reasonable to hypothesize that GEM is the main species initially taken up by lichens. Later,  $Hg^0$  can be accumulated as is or biotransformed into ionic mercury and organomercury compounds. We studied mercury thermospeciation in the *Parmelia caperata* lichens, collected in remote areas of South Africa to determine if the lichens contain elemental and bound mercury. The principle of thermospeciation is based on the detection of mercury atoms releasing from a sample during its gradual heating. This approach enables one to reveal mercury species having different bond energy with matrix. Determination of mercury thermospecies has been performed with a RA-915+ Zeeman mercury analyser with PYRO-915 attachment (Lumex Instruments) by direct mercury evaporation from dry lichens samples without any chemical pre-treatment. It was found that analytical signal of mercury from freshly collected lichens consists of two peaks. One appears in low temperature range of 30-120°C, which is formed by elemental mercury, and the other one, within 120-360°C, can be attributed to a stable compound of  $Hg^{2+}$  formed in lichens. On the average, the initial part of  $Hg^0$  in lichens was found to be approximately 10% ( $13.2 \text{ ng g}^{-1}$ ) of total mercury ( $136 \text{ ng g}^{-1}$ ) and can be observed only in the first few days after sample collection, because it steadily fade away in few days. The results of the present research open a new approach in studies on mercury species in lichens.

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## Food Safety implications of Polluted Water in South Africa

Cheryl McCrindle<sup>\*A</sup>, Mathapelo Seopela<sup>B</sup>, Abayneh Ambushe<sup>C</sup>, Kebede Mekkonen<sup>D</sup>, Rob McCrindle<sup>B</sup>

<sup>A</sup>School of Health Systems and Public Health, Faculty of Health Sciences, University of Pretoria, South Africa;

<sup>B</sup>Department of Chemistry, Tshwane University of Technology, P/B X680, Pretoria, 0001, South Africa;

<sup>C</sup>Department of Chemistry, University of Johannesburg, South Africa; <sup>D</sup>Department of Chemistry, Mekelle University, Ethiopia.

\*cheryl.mccrindle@gmail.com

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**ABSTRACT:** Water plays a major role in food safety of animal products like meat and milk, as well as edible crops, especially where toxic levels of elements are present. Rapid urbanization together increased mining and industrial activities have resulted in the water systems of South Africa to become polluted. The pollution may pose a risk to the communities making use of the water for agriculture and drinking. Five aquatic systems were investigated to determine the levels of mineral pollution. The concentration of a number of elements was determined by inductively coupled plasma-optical emission spectrometry and mass spectrometry. Levels of the same elements were then determined in products obtained from use of the water. These included vegetables, fish and meat. Peat used in the production of mushrooms was also investigated. The concentrations of the elements were in most cases at the level that intervention might become necessary, but currently the risk of using the water is minimal. The level of phosphates in a dam near Pretoria (Bon Accord Dam) continues to be high (22.7 mg/L) making the dam hypertrophic. Elements that were well above recommended levels in Loskop Dam were boron, iron and manganese (11000, 23100 and 447 mg/kg, respectively in sediment). The fish and meat proved to contain no elements above regulations levels, but the peat contained cadmium (1.00 mg/kg), which is above the maximum of 0.3 mg/kg.

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## Rare Earth Elements Determination in Crude Oil and Fractions by Electrothermal Vaporization-Inductively Coupled Plasma Mass Spectrometry

Fabio A. Duarte, Jussiane S. Silva, Alessandra S. Henn, Paola A. Mello, Cezar A. Bizzi, Erico M. M. Flores\*

Departamento de Química, Universidade Federal de Santa Maria, Santa Maria, RS, Brazil, 97105-900

\*ericommf@gmail.com

**ABSTRACT:** Information about the concentration of rare earth elements (REE) in crude oil and its fractions is of great importance for petroleum industry because. Generally, the determination of REE by inductively coupled plasma mass spectrometry (ICP-MS) requires digests with low carbon content and low acidity and, as a consequence, high efficiency sample preparation methods are required. However, digestion of crude oil is not a simple task. In the present work, an alternative method based on the use of electrothermal vaporization (ETV) system coupled to ICP-MS was developed for REE determination in crude oil. An ETV system (model ETV-4000c, Spectral Systems, Germany) with Freon R-12 was used. It was coupled to an ICP-MS equipment (model Elan DRC II, Perkin Elmer-SCIEX, USA). Experimental conditions were evaluated and the following conditions were selected: 700 and 2200 °C for pyrolysis and vaporization temperatures, respectively; 6 mg of citric acid as carrier aid; 0.35 L min<sup>-1</sup> for both bypass and carrier gas flow-rates; 2 mL min<sup>-1</sup> of Freon R-12 flow rate; and up to 5 mg of sample mass. Under the selected conditions, memory effects were minimized and external calibration was possible by using reference solutions showing the simplicity of the proposed method. Accuracy was investigated by comparison of REE determination by using an ultrasonic nebulizer (USN) system coupled to ICP-MS equipment after microwave-assisted wet digestion with nitric acid. The values obtained by ETV-ICP-MS and by USN-ICP-MS for crude oil, residues of atmospheric distillation (RAT) and residues of vacuum distillation (RV) were in good agreement. Regarding to the limits of detection (LODs) for REE, they ranged from 0.01 to 1.8 ng g<sup>-1</sup>, being lower than those obtained by USN-ICP-MS and considered as suitable for the determination of REE in the evaluated samples. The direct solid sampling ETV-ICP-MS method allowed the simultaneous determination of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y in crude oil, RAT and RV without previous sample digestion, avoiding the use of concentrated acids and minimizing the generation of laboratory residues.

## Endocrine Disrupters in Dolphins from the Brazilian Coast

Ricardo Lavandier<sup>A</sup>, Rosalinda Montone<sup>B</sup>, Satie Taniguchi<sup>B</sup>, Salvatore Siciliano<sup>C</sup>, Natalia Quinete<sup>D</sup>,  
Isabel Moreira<sup>\*A</sup>

<sup>A</sup>Departamento de Química, Pontifícia Universidade Católica, Rio de Janeiro, Brazil; <sup>B</sup>Instituto de Oceanografia, Universidade de São Paulo, São Paulo, Brazil; <sup>C</sup>Instituto Oswaldo Cruz, FIOCRUZ, Rio de Janeiro, Brazil; <sup>D</sup>RWTH, Aachen University, Germany.

\*isabel@puc-rio.br

**ABSTRACT:** Endocrine disrupters are organic or inorganic substances that may interfere with the hormonal system and pose a risk to humans and wildlife. Some of them such as polychlorinated biphenyls (PCBs) and polybrominated diphenylethers (PBDEs) are on the list of Persistent Organic Pollutants (POPs). They persist in the environment and are easily transported over long distances through the atmosphere and ocean currents. They are able to bioaccumulate in fat tissues and biomagnify along the food web. Dolphins are long-lived top predators very sensitive to environmental changes and may accumulate high concentrations of organic pollutants through bioaccumulation and biomagnification processes. They have been considered good bioindicators of aquatic contamination. The aim of the present work was to know the level of contamination by PCBs and PBDEs in dolphins incidentally caught in fishing nets in the Brazilian southeastern coast. These dolphins belong to two different species: *Tursiops truncatus* and *Stenella frontalis*. About 1.0 g of sample tissue (liver) was used for the chemical analysis. The analytical procedure was performed based on an Ultra Turrax extraction followed by clean-up and chromatographic analysis (GC/MS).  $\Sigma$ PCBs ranged from 3078 ng g<sup>-1</sup> to 15306 ng g<sup>-1</sup> (lipid weight) in *Tursiops truncatus* and from 6091 ng g<sup>-1</sup> to 29138 (lipid weight) in *Stenella frontalis*.  $\Sigma$ PBDEs varied from 331 ng g<sup>-1</sup> to 865 ng g<sup>-1</sup> (lipid weight) in *Tursiops truncatus* and from 397 ng g<sup>-1</sup> to 1686 ng g<sup>-1</sup> (lipid weight) in *Stenella frontalis*. PCB 153, 138 and 180 were the major PCB congeners detected in both species. In addition, BDE 47 was the major congener found in both species. The contamination patterns suggest the previous use of Aroclor 1254, 1260 and Penta-BDE in Brazil. PCBs and PBDEs were never produced in Brazil. Today PCBs are globally banned in accordance with the Stockholm Convention of 17 May 2004, but most of the transformer oils still in use in Brazil may contain PCBs imported from German and U.S.A. The concentrations of PCBs and PBDEs found in this study are of great concern (mainly in relation to PCBs), suggesting the presence of a source of contamination in the Brazilian southeastern coast and representing a risk to these cetacean species.

## Micro-Raman and SEM-EDX application to evaluate the nature of cluster particles present in Secondary Marine Aerosol highly influenced by anthropogenic emissions.

Héctor Morillas<sup>\*A</sup>, Iker Marcaida<sup>A</sup>, Maite Maguregui<sup>B</sup>, Cristina García-Florentino<sup>A</sup>, Urko Balziskueta<sup>C</sup>, Juan Manuel Madariaga<sup>A</sup>

<sup>A</sup>Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country UPV/EHU, 48080 Bilbao, Basque Country, Spain; <sup>B</sup>Department of Analytical Chemistry, Faculty of Pharmacy, University of the Basque Country UPV/EHU, 01080 Vitoria-Gasteiz, Basque Country, Spain; <sup>C</sup>Department of Geography, Prehistory and Archaeology, University of the Basque Country UPV/EHU, 01080, Vitoria-Gasteiz, Basque Country, Spain.

\*hector.morillas@ehu.eus

**ABSTRACT:** The marine aerosol constitutes one of the most important natural aerosols from the Earth and comprises primary and secondary aerosol components. The primary marine aerosol (PMA) is formed due to the interaction of the wind on the ocean surface. The result of this interaction is the mechanical production of the sea spray (inorganic sea salt and organic matter). Sea spray, is produced when the bubbles from the generated whitecap burst. This process originates a jet of saline drops commonly known as sea spray aerosol (SSA). This aerosol carries particles of submicrometre size and up to a few micrometers. One of the physical characteristics of the sea aerosol is the size of its suspended particles ( $>1\ \mu\text{m}$ ), which depends on the wind speed, sea-air water transfer, etc. Apart from this, the SSA has a key role in chemical reactions such as the coupled cycles of sulfate-sea salt and nitric acid-sea salt. The secondary marine aerosol (SMA) production consists on cluster particle formation resulting from gas to solid particle conversion. The first step consists in the new particle formation via the nucleation of 0.5–1 nm stable clusters. Once these clusters are formed, they can grow to larger sizes via condensation. The second step consists in the clusters growing via different heterogeneous reactions and aqueous phase oxidation of dissolved gases in existing aerosol particles. According to the different sizes that aerosol particles can raise, marine aerosol clusters can have 1000–10000 nm volume diameter size. Although the main mass fraction of marine aerosol is inorganic sea salt, organic matter is present and can also contribute to the overall mass. The most abundant salt carried on marine aerosol is sodium chloride, but other types of chemical compounds like sulfates and nitrates can also be present. Apart from these, other ions are also present in a suspended way such as  $\text{Ca}^{2+}$ ,  $\text{K}^{+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Sr}^{2+}$ ,  $\text{NH}_4^{+}$ ,  $\text{HCO}_3^{-}$  and  $\text{Br}^{-}$ . Usually, organic matter has also a high importance because it represents around the 10% of marine aerosol. In this work, airborne particulate matter was sampled in a marine environment (Getxo, Spain) highly influenced by anthropogenic emissions (industry, maritime port, etc.). A self-made passive sampler (SMPS) including several aluminum pin stubs was exposed in an historical construction (Punta Begoña Galleries) located in this town and placed in front of the sea. The particles deposited on the pin stubs were characterized directly by micro-Raman spectroscopy and SEM-EDS, without any sample preparation. Thanks to the combination of these techniques, marine cluster salts such as mascagnite  $((\text{NH}_4)_2\text{SO}_4)$ , hexahydrate  $(\text{MgSO}_4 \cdot 6\text{H}_2\text{O})$ , epsomite  $(\text{MgSO}_4 \cdot 7\text{H}_2\text{O})$ , syngenite  $(\text{K}_2\text{Ca}(\text{SO}_4) \cdot \text{H}_2\text{O})$ , glauberite  $(\text{CaNa}_2(\text{SO}_4)_2)$ , anhydrite  $(\text{CaSO}_4)$ , nitratine  $(\text{NaNO}_3)$ , niter  $(\text{KNO}_3)$  and other halite clusters with low content of different ions such as  $\text{Ca}^{2+}$ ,  $\text{K}^{+}$ ,  $\text{Mg}^{2+}$  etc were identified. These cluster salts can be deposited on the surface of building materials following a dry deposition process. The deposited particles can react (some are acids) with the Built Heritage material, promoting the formation of deterioration products that during time jeopardize the loss of material in the building.



## Direct Speciation Analysis of Arsenic in Wine, Beer and Apple Juice by Hydride Generation- Cryotrapping- Atomic Absorption Spectrometry

Aneta Fajgarová<sup>A,B</sup>, Tomáš Matoušek<sup>\*A</sup>

<sup>A</sup>Department of Trace Element Analysis, Institute of Analytical Chemistry of the CAS, v. v. i., Brno, Czech Republic; <sup>B</sup>Department of Analytical Chemistry, Faculty of Science, Charles University in Prague, Czech Republic.

\*matousek@biomed.cas.cz

**ABSTRACT:** Arsenic is an element known for his chronic toxicity. Of many arsenic species, inorganic arsenic (iAs) is of prime interest. However, beside iAs, food typically contains significant concentrations of organic arsenic species, most prominent dimethylarsinate and arsenobetaine, which are less toxic or not toxic at all. Accurate assessment of dietary exposure to inorganic arsenic in the population requires development of analytical methods capable of speciation analysis in food matrix.

Recently, several reports showed elevated arsenic content in beverages, especially wine and fruit juices, and attracted significant public attention. There is no legislative regulation of arsenic in beverages at present. In most countries including EU and the Czech Republic, there is only drinking water limit for total arsenic ( $10 \mu\text{g l}^{-1}$ ). In the Czech Republic, there used to be a maximum admissible levels of As in fruits and fruit juices set by Regulation 305/2004 Coll as  $0.2 \text{ mg kg}^{-1}$ , but this regulation has not been valid since 2012. In the USA, in 2013 the Food and Drug Administration published draft guidelines for iAs in apple juice of  $0.01 \text{ mg kg}^{-1}$ . For wine, the regulation for total arsenic currently in use is  $200 \text{ mg l}^{-1}$ , set by the International Organization of Vine and Wine.

A method for analysis of toxicologically important arsenic species in beverages will be presented, based on hydride generation with cryotrapping (HG-CT) and AAS detection with a quartz multiatomizer. This method, with an automated cryotrap has been so far validated for a number of matrices, eg. urine, cell lysates, tissue homogenate or rice extracts. The method allows sampling of a slurry; therefore sample preparation involves only 5 times dilution of beer and apple juice (unfiltered) or 10 times dilution of wine with addition of L-cysteine for prereduction of As species. Foaming in the HG is suppressed by addition of Antifoam B to the reductant solution.

Slopes of calibration graphs in sample matrix spiked with iAs, monomethylarsonate (MAs) and dimethylarsinate (DMAs) at  $0.5\text{-}2 \mu\text{g l}^{-1}$  As levels agreed with the slopes in aqueous solutions. Limits of detection for the As species were  $0.15\text{-}0.3 \mu\text{g l}^{-1}$  As in beer and apple juice, and  $0.3\text{-}0.6 \mu\text{g l}^{-1}$  As in wine, sufficiently low with regards to target value of  $10 \mu\text{g l}^{-1}$ .

Speciation analysis in 11 samples of red wines, 6 samples of beer and 8 samples of apple juice was performed. Only single sample of apple juice contained more than  $10 \mu\text{g l}^{-1}$  iAs. In all samples the MAs a DMAs concentrations were below limit of detection. Found arsenic contents were in good agreement with total As content determined by ICP-MS after microwave digestion in  $\text{HNO}_3$ .

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## Essential and Toxic Metal Contents in Smoked Meat Products available on the Polish Market

Agnieszka Nawrocka, Maciej Durkalec, Mirosława Kmiecik and Andrzej Posyniak

Department of Pharmacology and Toxicology,  
National Veterinary Research Institute Al. Partyzantów 57, Pulawy, Poland

\*agnieszka.nawrocka@piwet.pulawy.pl

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*Evaluation of chemical elements content in food of animal origin is a very important element in terms of protection of human health. The source of many elements in food may be natural geological process releases metals deposited at lithosphere to the water, soil and air. Consequently various amounts of toxic metals are present in meat and meat products. The concentration of essential elements in meat products can be diverse and depends on the type of meat, used additives and production processes. The aim of this study was to assess the total concentrations of essential (Cu, Cr, Fe, Mn, Mo, Se and Zn) and toxic (As, Cd, Pb) elements in traditional smoked sausages and meat products commercially available on the Polish market. Determination of selected elements was carried out by quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS) after microwave digestion of samples with nitric and hydrochloric acids and hydrogen peroxide solution.. The contribution of smoked meat products in recommended daily allowances of micronutrients (RDA) was estimated. The consumption of a portion of 50g smoked meat products can be a valuable source of some micronutrients, especially Cr (23% RDA), Cu (12% RDA), Se (14% RDA) and Zn (13% RDA). Obtained results were also compared to the maximum levels of toxic metals in food defined in the Commission Regulation No. 1881/2006. Considering low concentrations of toxic elements in smoked meat and sausages (As - 0.003; Cd - 0.002; Pb - 0.041 mg/kg of wet weight,) consumption of these products should not pose a risk to consumers. Acknowledgements: The research was supported by KNOW (Leading National Research Centre) Scientific Consortium "Healthy Animal - Safe Food", decision of Ministry of Science and Higher Education No. 05-1/KNOW2/2015.*

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## Determination of antimony and tin in beverages using inductively coupled plasma-optical emission spectrometry after ultrasound-assisted ionic liquid dispersive liquid-liquid phase microextraction.

Tshimangadzo S. Munonde, Nobanathi W. Maxakato, Philiswa N. Nomngongo\*

<sup>a</sup>Department of Applied Chemistry, University of Johannesburg, Doornfontein Campus, P.O. Box 17011, Johannesburg, 2028, South Africa; <sup>b</sup>Analytical Facility, University of Johannesburg, P.O. Box: 524, Auckland Park 2006, South Africa.

\*pnnomngongo@uj.ac.za

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**ABSTRACT:** The article describes a method for preconcentration and speciation of Cr(III) and Cr(VI) in river waters. It is based on ultrasound-assisted magnetic solid phase extraction employing a nanocomposite prepared from magnetite nanoparticles, manganese oxide and alumina oxide, and then functionalized with [3-(2-aminoethylamino) propyl] trimethoxysilane (AAPTMS). By taking advantage of the oxidative properties of MnO<sub>2</sub>, the Fe<sub>3</sub>O<sub>4</sub>@MnO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> nanocomposite was used for the preconcentration of total chromium. The AAPTMS-modified nanocomposite, in turn, is selective for Cr(VI). The concentrations of Cr(III) can be calculated as the difference between total chromium and Cr(VI). The preconcentrated chromium species were quantified using ICP-OES. The method was optimized using response surface methodology (RSM). Under optimal conditions, the limit of detection and quantification are 20 and 50 pg mL<sup>-1</sup>, respectively. The intraday and interday precisions of the method, expressed in terms of relative standard deviation, are 2.6 and 4.9 %, respectively. In addition, the effects of potentially interfering ions were examined. The method was successfully applied to the speciation of chromium in spiked river water and a certified reference material (CRM).

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## Preconcentration and speciation of chromium in river water using inductively coupled plasma-optical emission spectroscopy after ultrasound-assisted magnetic solid phase extraction.

Tshimangadzo S. Munonde, Nobanathi W. Maxakato, Philiswa N. Nomngongo \*

<sup>a</sup>Department of Applied Chemistry, University of Johannesburg, Doornfontein Campus, P.O. Box 17011, Johannesburg, 2028, South Africa; <sup>b</sup>Analytical Facility, University of Johannesburg, P.O. Box: 524, Auckland Park 2006, South Africa.

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## Normalization of LIBS spectra using acoustic and total emission signal

Karel Novotný <sup>\*A,B,C</sup>, Aleš Hrdlička <sup>B,C</sup>, Eva Pospíšilová <sup>A</sup>, Jakub Píše <sup>A</sup>, Pavel Pořízka <sup>C,D</sup>, Jozef Kaiser <sup>C,D</sup>

<sup>A</sup>Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, Brno, 61137, Czech Republic;

<sup>B</sup>Masaryk University, Central European Institute of Technology, Kamenice 753/5, Brno, 62500, Czech Republic;

<sup>C</sup>AtomTrace a.s., Vědecko-technický park profesora Lista, Kolejní 9, Brno, 61200, Czech Republic;

<sup>D</sup>Brno University of Technology, Central European Institute of Technology, Purkyňova 123, Brno, 61200, Czech Republic.

\* codl@sci.muni.cz

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*ABSTRACT: Since that laser-induced plasma emission is extremely dependent on the initial conditions, significant fluctuations occur even with constant parameters and a strict control of the experimental setup. Laser-Induced Breakdown Spectroscopy (LIBS) signal intensity suffers from the specific influences resulting from the laser ablation and plasma processes which affect the accuracy and precision of analytical result. To improve reproducibility and accuracy utilization of alternative normalization procedure based on plasma monitoring is possible. In our study for careful correction of the pulse-to-pulse changes of sampling parameters acoustic and total emission were used. Correlation between total optical emission and acoustic signal is demonstrated and effect of the laser pulse energy, focusing and nature of sample is discussed. Normalization of LIBS spectra using acoustic and total emission signal in bulk analysis, depth profiling and surface mapping is presented.*

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## Analysis of Scale Deposition in Oil Pipes using X-Ray Microfluorescence Imaging Technique

Davi F. Oliveira<sup>\*A,C</sup>, Carla A. Marinho<sup>B</sup>, Marcelino J. Anjos<sup>A,C</sup>, Ricardo T. Lopes<sup>C</sup>

<sup>A</sup>Physics Institute, State University of Rio de Janeiro, Rio de Janeiro, Brazil; <sup>B</sup>Leopoldo A. Miguez de Melo Research Center, CENPES/PETROBRAS, Rio de Janeiro, Brazil; <sup>C</sup>Nuclear Instrumentation Laboratory, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil.

\*davi@lin.ufrj.br

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**ABSTRACT:** The occurrence of scales in pipes and equipment has been reported since the 30's and consists in one of the most relevant problems in the oil prospecting field. The formation of scales (metal sulphates, calcium carbonates and silicates) occurs when incompatible types of water (injected seawater and formation water) are mixed in the reservoir, unavoidably undergoing chemical interaction followed by mineral precipitation. Scales limit and sometimes block oil and gas production by plugging the oil producing formation matrix or production lines and equipment, consequently impairing fluid flow. Due to that, there is a need for determining the way such materials are deposited within the piping system in order to optimize the methods used for preventing and removing scales. The purpose of this work is to use  $\mu$ XRF in order to identify the elements and determine their distribution in scale samples from obstructed oil pipes. The samples were extracted from scales found in steel and composite pipes, coated in resin and then sliced in thin layers of 1.35 mm in thickness, maintaining their original position in the interior of the pipe. The samples were analyzed through  $\mu$ XRF with a Bruker M4 Tornado equipment. The measurements were carried out in vacuum with a step size of 200  $\mu$ m and a counting live time of 10 ms/pixel, resulting in a 2D distribution map for each element of the samples. As a result of this process, the elements Al, Si, S, Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, Br, Sr, Ba and Pb were found in the samples. In the scale samples extracted from steel pipes, the element Cr was also present due to its utilization to inhibit corrosion. The images generated in the experiment showed how the above-mentioned elements were spread throughout the layers formed by the deposition of scales within the pipes. It was possible to observe that the elements S, Sr and Ba were found in very well-defined layers, pinpointing the deposition points for  $\text{BaSO}_4$  and  $\text{SrSO}_4$ . The distribution of the elements Sr and Ba presented similar behavior due to the chemical affinity they share. The element Cr was found in several layers, in an also well-defined manner, denoting the occasions in which the corrosion inhibitor was injected. High intensities of the element Fe were found in a homogeneously distributed manner across the samples. The presence of the element Ca, whose distribution was similar to the one of sulphur, indicates the presence of  $\text{CaSO}_4$ . Well-defined layers of Ca without the presence of S were observed particularly in oil pipes made of composite material, indicating thus that  $\text{CaCO}_3$  is the predominant scaling type for this type of pipe. The results have shown that it is possible to identify the elements contained in scaling samples, as well as to determine their distribution across the samples. In this way, it would be possible to predict what kind of scaling will likely be formed in different types of pipes, thus allowing the optimization of prevention and removal methods of such materials.

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## Determination of Heavy Metals in Beer using ICP-MS Spectrometry

Uwe Oppermann<sup>\*A</sup>, Ludivine Fromentoux<sup>B</sup>, Jan Knoop<sup>A</sup>, and Jürgen Schram

<sup>A</sup>Shimadzu Europa GmbH, Analytical BU, 47269 Duisburg, Germany; <sup>B</sup>Shimadzu France SAS, Marne La Vallée, France; University of applied Sciences, Krefeld, Germany.

\*uo@shimadzu.eu

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*ABSTRACT: Beer is probably one of the oldest alcoholic drinks in the world. In fact, Chinese and Egyptians already made beer in 4000 years BC. In Europe, beer was the Celts' famous beverage throughout the ancient times. In order to assure standards regarding quality, freshness, appearance and flavor, much regulation exists in Europe since the early XVIth century ("Reinheitsgebot" in 1516 in Germany; royal decree of 1495 in France ...). Louis Pasteur, one of the most famous 19th century scientist, started his career by researching beer process improvement. Nowadays, with wide interest in the diversity and variety of beers, more than 6500 breweries exist in Europe. The quality standards for beer analysis are defined by the Central European Commission for Brewing Analysis (MEBAK) and the European Brewery Convention (EBC), representing technical and scientific interests of the brewing sector in European countries. These regulations include the determination of numerous elements (e.g. As, Ca, Cu, Na, K ...), anions (such as nitrate and sulfite) as well as organic components (ethanol, glycerine) and others (pesticide residues). In order to maintain the highest level of quality, some chemical investigations have to be performed, using different analytical techniques to quantify all the potential contaminants. For simultaneous quantitative determination of the inorganic elements in beer, ICP-MS is the most preferable tool for quality control because of its high sensitivity (trace detection), wide dynamic range and high sample throughput. All measurements have been done on the Shimadzu ICPMS-2030 which is an easy to operate and fast system meeting these requirements. The quantitation results demonstrate that ICPMS-2030 is able to simultaneously quantify the various elements present in beer samples.*

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## The Solid Phase Extraction of Some Trace Metals Using Graphene Nanoplatelets by HR-CS AAS

Nil Ozbek <sup>A</sup>, Aslı Baysal <sup>B</sup>

<sup>A</sup> Department of Chemistry, Istanbul Technical University, Maslak, Istanbul, Turkey; <sup>B</sup> Health Services Vocational School of Higher Education, T.C. Istanbul Aydin University, Kucukcekmece - Istanbul, Turkey

\*nil.ozbek@itu.edu.tr

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**ABSTRACT:** In order to concentrate a trace analyte above its limit of detection as well as to eliminate the interferences, a separation/enrichment technique is necessarily applied prior to its determination. Solid phase extraction is the most common technique to separate and enrich the trace analytes prior to their determination. For this purpose, functional polymers, ion-exchangers, silica gels, nano particles, biological materials, industrial wastes, bacterias etc. have been used as a sorbent applying batch or column techniques. In all those applications, the analytes have been collected on the sorbent and then recovered with an appropriate eluate successfully and practically. In this study, a new nanostructure which is graphene nanoplatelets used for the separation and enrichment of cadmium, chromium, nickel, copper and lead prior to its determination by atomic absorption spectrometry was described. For this purpose, analyte elements were collected on sorbent. The effects of experimental conditions with regards to the amount of sorbent, pH of sample, concentration and kind of eluent, foreign ions, and retention-elution parameters on the recovery of the analyte were investigated. Using the proposed technique, the cadmium, chromium, nickel, copper and lead concentrations in various water samples (sea water, waste water, tap water) could be practically and rapidly removed and enriched in the range of 95% confidence level. The detection limit of the described method for cadmium, chromium, nickel, copper and lead using sample-matching blanks were calculated. The proposed technique was fast, simple, and economic.

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## Determination of Pb, Zn and Cd in soil samples by means of total reflection X-ray fluorescence analysis

Fabjola Bilo <sup>A</sup>, Laura Borgese <sup>A</sup>, Rogerta Dalipi <sup>A</sup>, G.Pardini<sup>B</sup>, E.Marguí<sup>\*C</sup>, Laura E. Depero <sup>A</sup>,

<sup>A</sup> INSTM & Chemistry for Technologies Laboratory, Department of Mechanical and Industrial Engineering, University of Brescia, Via Branze, 38, 25123, Brescia, Italy; <sup>B</sup> Department of Chemical Engineering, Agricultural and Food Technology, University of Girona, C/M.Aurèlia Campmany 61, 17003 Girona, Spain; <sup>C</sup> Department of Chemistry, University of Girona, C/M.Aurèlia Campmany 69, 17003 Girona, Spain

\*eva.margui@udg.edu

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**ABSTRACT:** *The monitoring of metal concentration in soils is of significance in many environmental studies. In this sense, fast analytical methodologies which entail simple sample preparation and low-cost analysis are desired. In the present contribution, the possibilities and drawbacks of total reflection X-ray fluorescence spectrometry (TXRF) have been evaluated for the simultaneous determination of Pb, Cd and Zn in soils. An easy and rapid sample preparation procedure consisting in suspending 20 mg of fine ground soil sample in 1 mL of Triton 1% in water (v/v) showed to be suitable for the determination of the aforementioned elements at concentration levels below 10 mg·kg<sup>-1</sup>, which is in most cases suitable according to the metals thresholds for different soil uses by EU Directive 2010/75/UE ([Pb]:60-550 mg·kg<sup>-1</sup>, [Zn]:110-1000 mg·kg<sup>-1</sup> and [Cd]:0.6-55 mg·kg<sup>-1</sup>). Internal standardization and external calibration using laboratory-made soil standards were used as quantitative approaches. Good agreement was obtained between TXRF results obtained for soil reference materials analysis and certified/indicative values and, in most cases, no significant differences were found at 95% confidence level. Despite the fact that the total precision for soil suspension measurements was higher (RSD: 15-20%) than that associated with other methodologies involving soil analysis, the benefits of this fast and less time-consuming analytical approach make it desired for this type of environmental studies. An additional advantage of the proposed methodology is the possibility to get information of other elements present in the soil taking into account the multielemental capability of TXRF spectrometry. As a study case, TXRF method was applied to determine Pb, Zn and Cd in several soil samples from an abandoned mining area located in the Northeast of Spain. Results obtained were compared with those obtained by microwave acidic digestion and inductively coupled plasma emission spectroscopy.*

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## Presence, mobility and bioavailability of toxic metals in soil, vegetation and streamwater around a ceased Pb-Sb factory (Sant Llorenç d'Hortons, Barcelona, Spain).

S.Mykolenko<sup>A</sup>, V.Liedienov<sup>A</sup>, M.Kharytonov<sup>A</sup>, I.Queral<sup>B</sup>, M.Hidalgo<sup>C</sup>, E.Marguí<sup>C</sup>, G.Pardini<sup>\*D</sup>

<sup>A</sup> Dnipropetrovsk State Agrarian & Economic University 25, Voroshilov str. Dnipropetrovsk 49027, Ukraine; <sup>B</sup> Institute of Environmental Assessment and Water Research, IDAEA-CSIC, Jordi Girona 18-26, 08034, Barcelona, Spain; <sup>C</sup> Department of Chemistry, University of Girona, C/M.Aurèlia Campmany 69, 17003 Girona, Spain; <sup>D</sup> Department of Chemical Engineering, Agricultural and Food Technology, University of Girona, C/M.Aurèlia Campmany 61, 17003 Girona, Spain

\*giovanni.pardini@udg.edu

**ABSTRACT:** Different industrial activities worldwide have strongly contributed to the contamination of extended areas in and around mining and industrial sites, especially when lacking of specific Directives for environmental protection. The aim of the present contribution was to study the presence, mobility and bioavailability of toxic metals in soil, vegetation and streamwater around a ceased industrial factory located in Spain (Sant Llorenç d'Hortons, Barcelona), devoted to the recycling of batteries from car industry with the main purpose to recover pure Pb and Sb. For that, a multianalytical approach involving the use of several spectroscopic methodologies was used. Metal and metalloid (As, Cd, Cu, Ni, Mn, Pb, Sb, Se, Sn and Zn) concentrations in soil samples, determined by microwave digestion in combination with inductively coupled plasma optical emission spectroscopy (ICP-OES), were extremely high in soils from the landfill of hazardous wastes disposed during the industrial activity and most element concentrations exceed the thresholds for soil uses according to the Spanish Royal Decree 9/2005. The high presence of Pb ( $485 \text{ mg}\cdot\text{kg}^{-1}$ ) in soils collected almost 1 km far away from the focal point of contamination may suggest metal transport by wind as a possible vehicle of contamination. In order to evaluate the mobile fraction of the investigated metals in soils, a sequential extraction procedure was applied to study the soluble fraction (by water extraction), the readily available fraction (by  $\text{KNO}_3$  extraction) and the complexed fraction by using EDTA to simulate the effect of organic matter when entraps metals into organic molecules. Absolute percent of metal mobile fraction expressed as the total of the three subsequent extractions was substantially low with respect to total metal content ( $<5\%$ ). However, these values account for a considerable metal content potentially available to plant and animals thus threatening the whole ecosystem under study. In fact, anomalous metal concentrations in comparison to control specimens were found in different vegetal tissues (roots, stems, leaves and flowers) of native plant species (*Dittrichia viscosa*, *Foeniculum vulgare*, *Helychrisum stoechas*) sampled in the contaminated area. For instance, *Helychrisum stoechas* results allowed establishing its strong ability for phytostabilization as the highest values of As, Cd, Cu, Mn, Ni, Pb, Sb and Sn were found in the root and decreased when analyzing the aerial parts of these plants. Results may also indicate that *Dittrichia viscosa* was able to absorb the highest concentration of Pb reaching a mean of  $1700 \text{ mg}\cdot\text{kg}^{-1}$  in stems. This plant may also be considered for phytoremediation technologies as in most cases it tends to concentrate the metals in the aerial parts. Final, multielemental analysis of waters sampled in the contaminated area by total reflection X-ray fluorescence spectrometry (TXRF) showed that even this ecological compartment may be affected by the dispersion of toxic metals with Sb and Pb values up to  $2.0 \text{ mg}\cdot\text{L}^{-1}$  and  $2.6 \text{ mg}\cdot\text{L}^{-1}$ , respectively.

## Electron density and temperature distribution in expanding laser-induced plasma

Christian G Parigger<sup>\*A</sup>, Ghaneshwar Gautam<sup>A</sup>, Chris Helstern<sup>A</sup>, Kyle Drake<sup>A</sup>

<sup>A</sup>University of Tennessee Space Institute, Center for Laser Applications, 411 B.H. Goethert Parkway, Tullahoma, TN 37388, U.S.A.

\*cparigge@tennessee.edu

**ABSTRACT:** Q-switched, 150 mJ, 14 ns pulsed Nd:YAG laser radiation at the fundamental wavelength of 1064 nm is used to generate micro-plasma in a ultra-high-pure hydrogen and nitrogen gas mixture. The H<sub>2</sub> and N<sub>2</sub> ratio is 9 to 1 at pressure of  $1.21 \pm 0.03 \times 10^5$  Pa inside a chamber. Spatially and temporally resolved line-of-sight spectra of Stark-broadened hydrogen Balmer alpha, H <sub>$\alpha$</sub> , and beta, H <sub>$\beta$</sub> , lines are recorded using a Czerny-Turner type spectrometer and an intensified charge coupled device. The data are Abel inverted to determine the shell structure of electron density and temperature distributions [1].

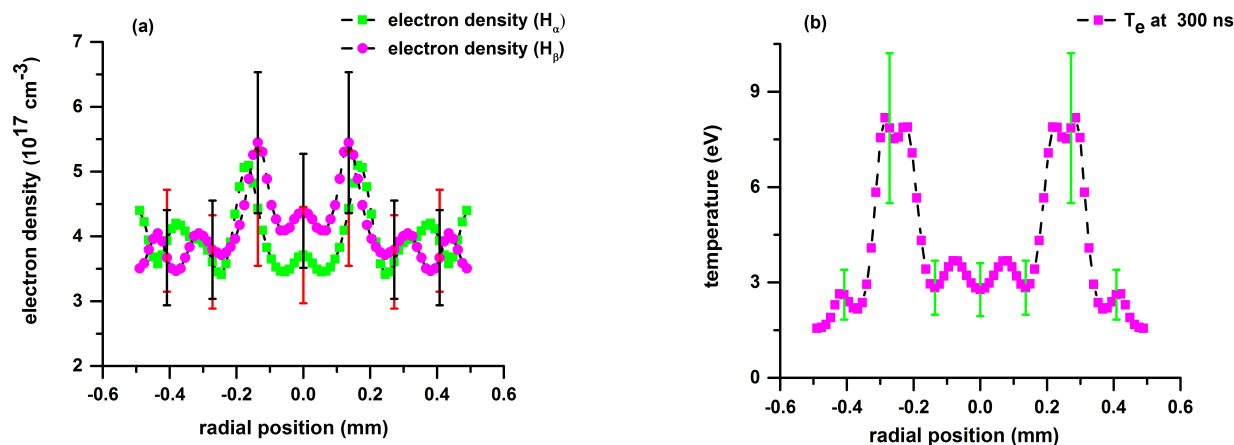


Figure 1: (a) Radial electron density and (b) temperature distribution at 300 ns time delay from optical breakdown. The measured hydrogen Balmer H <sub>$\alpha$</sub>  and H <sub>$\beta$</sub>  lines are used to determine [2] the spatial variation of electron density,  $N_e$ , and temperature,  $T_e$ . The radial temperature distributions are deduced from Boltzmann plots using H <sub>$\alpha$</sub>  and H <sub>$\beta$</sub>  lines [3-5]. The temperature in the central region of the plasma is found to be lower than found towards the outer region of the spherical ring or shell structure. The kernel expansion speed is close to the speed of sound in hydrogen gas and reveals high peak temperatures. The plasma expansion appears to be isentropic, characterized by  $T/N_e^{2/3} = \text{constant}$ , in agreement with previous hydrogen experiments [6,7].

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## The use of portable EDXRF setup with triaxial geometry for the study of liquid samples – Application to mine waters

Sofia Pessanha<sup>\*A</sup>, Maria Luisa Carvalho<sup>A</sup>, E. Marguí<sup>B</sup>, Ignasi Queralt<sup>C</sup>

<sup>A</sup>LIBPhys -Laboratório de Instrumentação, Engenharia Biomédica e Física da Radiação, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal; <sup>B</sup>Department of Chemistry, University of Girona, C/M.Aurèlia Campmany 69, 17003 Girona, Spain; <sup>C</sup> Institute of Environmental Assessment and Water Research, IDAEA-CSIC, Jordi Girona 18-26, 08034, Barcelona, Spain

\*sofia.pessanha@fct.unl.pt

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**ABSTRACT:** In this work, we will present the calibration of a portable Energy Dispersive X-Ray Fluorescence setup for the analysis of trace elements in liquid samples, using filter sample retainers. For this purpose, two different sample retainers will be used and the outcome will be compared. The used experimental setup was developing with orthogonal triaxial geometry between the X-ray tube beam, the secondary target, the sample and the detector. This geometry reduces the background of the measured spectra by reducing significantly the Bremsstrahlung produced in the tube through polarization in the secondary target and in the sample. Consequently, practically monochromatic excitation energy is obtained. In this way, a better peak-background ratio is obtained compared to similar devices leading to superior sensitivity. Different concentrations of certified reference materials were used to determine the limits of detection, mainly for transition metals, and to construct a calibration curve for further analytical runs. Mine water samples collected at abandoned Tinoca copper mine (Northern Alentejo region, Portugal) were analyzed using this analytical setup. Results have been compared with related EDXRF commercial benchtop instrumentation.

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## Enhancement of laser-induced breakdown spectroscopy signal by means of combination of pre-ablation and re-heating laser pulses

David Prochazka<sup>\*A,B,C</sup>, Jakub Klus<sup>A,B,C</sup>, Pavel Pořízka<sup>A,C</sup>, Jan Novotný<sup>A,B,C</sup>, Karel Novotný<sup>C</sup>, Aleš Hrdlička<sup>C</sup>, Jozef Kaiser<sup>A,B,C</sup>

<sup>A</sup>Materials Characterization and Advanced Coatings, Central European Institute of Technology, Purkyňova 656/123 Brno, Czech Republic; <sup>B</sup>Faculty of Mechanical Engineering, Brno University of Technology, Technická 2 Brno, Czech Republic; <sup>C</sup>AtomTrace, Kolejní 9 Brno, Czech Republic.

\*david.prochazka@ceitec.vutbr.cz

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*ABSTRACT: Using combination of two laser pulses in different geometrical and experimental arrangements in order to enhance laser-induced breakdown spectroscopy (LIBS) signal is well known and described practice. For orthogonal arrangement are used two possible approaches – pre-ablation (first laser pulse create air spark slightly above the sample surface) and re-heating (second pulse re-heat the plasma). In this work is researched the effect of combination of both approaches in triple pulse experiment. Two Nd:YAG lasers (first laser solely for material ablation and second double pulse laser for pre-heating and re-heating respectively) are used in orthogonal arrangement. The study is performed on metallic and non-metallic samples with emphasis on “hard to detect” elements. The experimental parameters such as interpulse delays, laser pulse energies and gate delay are optimized. The enhancement effect differs for different samples and elements respectively from units to tens relatively to single pulse measurement.*

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## Fast Detection of Adulteration in Honey using Laser-Induced Breakdown Spectroscopy and Neural Networks.

C. Rico, S. Manzoor, J.D. Rosales, J.O. Cáceres

Laser Chemistry Lab., Department of Analytical Chemistry, Faculty of Chemical Sciences, Complutense University, Avda. Complutense s/n, 28040, Madrid.

\*maririco@ucm.es

**ABSTRACT:** The system of quality assurance to control fraud, preserve the Protected Denomination of Origin (PDO) and special characteristics of honey is regulated by law [1]. The amount and relative proportion of the mineral elements such as Mg, Ca, K and Na in honey depends on several factors such as flowering, flowers type, climate, water availability and quality, soil type and the way in which the honey is elaborated and stored [2,3]. Laser induced breakdown spectroscopy (LIBS) has been a subject of research for the past few decades because of its unique features and wide variety of applications in various fields. In recent years, LIBS has become a powerful analytical tool because of its ability to carry out a rapid qualitative and quantitative analysis of different samples [4]. LIBS analyzes a sample by direct measurement of the atomic emission of the elements from a laser-induced plasma generated by the ablation of the sample, providing an immediate spectral fingerprint that is representative of its elemental composition. Moreover, the technique requires little or no sample preparation. Although there is a loss of molecular information in plasma, this technique has provided excellent results for the identification of many polymer organic compounds, explosives, and bacteria. The intensities of C, H, N, and O lines and the C/H, C/O, and C/N intensity ratios have been used for the classification of organic compounds [5]. In this work, a quick and cost effective method based on Laser Induced Breakdown Spectroscopy (LIBS) and Neural Networks (NN) has been developed and applied to the identification of the quality control and PDO of honey. The samples analyzed belonged to the most important Spanish PDOs. Instant identification of the samples was achieved using a spectral library, which was obtained by analysis of representative samples using a single laser pulse and treatment by NN. The results obtained allowed the identification of the honey tested with a certainty of above 98%. Single-shot measurements were enough for clear identification of the samples.

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## Calibration-free laser induced breakdown spectroscopy for the quantitative determination of soil nutrients

Daniel Riebe<sup>\*A</sup>, Stefano Pagnotta<sup>B</sup>, Toralf Beitz<sup>A</sup>, Hans-Gerd Löhmannsröben<sup>A</sup>, Vincenzo Palleschi<sup>B</sup>

<sup>A</sup>Physical Chemistry, University of Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany; <sup>B</sup>Applied Laser Spectroscopy Lab, ICCOM U.O.S. di Pisa – CNR – Via G. Moruzzi, 1 – 56124 Pisa, Italy

\*riebe@uni-potsdam.de

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**ABSTRACT:** The aim of precision agriculture is the optimization of crop growth by means of site-specific fertilizing recommendations and thus effective and ecofriendly soil management. Due to the expenses associated with traditional methods requiring sample collection and laboratory analysis, such technologies are still not in widespread use. Therefore, a field-deployed, sensor-based analysis system offering rapid, cost-effective and spatially-resolved fertilizer recommendations would be highly desirable. In such a system, laser-induced breakdown spectroscopy (LIBS) could be ideally suited to assessing elemental nutrient contents of soils. In addition to low cost, durability and small size, a reliable quantification procedure is a crucial requirement for such a system. However, a plethora of mechanical as well as chemical soil compositions may be encountered in nature. Therefore, the matrix dependence is the key challenge to be addressed in the application of LIBS for soil evaluation. One possible approach would be the creation of an extensive calibration database accounting for every important soil type. A much more elegant alternative could be the calibration free (CF) LIBS method. This method relies on the physical characterization of the plasma encountered during the LIBS process. Thus, plasma temperature and electron densities are calculated and used to infer the initial concentrations in the sample. The focus of this work was the establishment of a LIBS method for soil analysis in a laboratory environment for future field application.

A commercial echelle spectrometer (LTB Aryelle Butterfly) was used in combination with a Nd:YAG laser (Spectra-Physics Quanta-Ray,  $\lambda = 355$  nm). Dried soil samples were ball milled and pressed into pellets.

Natural soil samples of various origins and soil types (sand, loess, clay) were used to characterize the matrix dependence of the LIBS spectra. Reference samples were prepared by adding defined amounts of the target elements to the soils (standard addition). Signals not superimposed by peaks of other elements were identified for each element. The reference samples also provided calibration curves for the respective soil type when the initial concentrations in the soils were taken into account. The same reference samples were used for testing and optimizing as well as verifying the CF-LIBS method. Both calibration-based and CF-LIBS methods were subsequently applied to soil samples collected in a narrow-grid soil survey on an agricultural field.

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## Molecular femtosecond LIBS compared to excitations with longer pulse durations

Anne-Sophie Rother, Peter Kohns, Georg Ankerhold\*

University of Applied Sciences Koblenz, RheinAhrCampus,  
Joseph-Rovan-Allee 2, 53424 Remagen, Germany

\*[ankerhold@hs-koblenz.de](mailto:ankerhold@hs-koblenz.de)

**ABSTRACT:** Aside from atomic and ionic lines, also a broad band emission of radicals and molecules occurs with a temporal delay within the microsecond range after irradiating the laser pulse. This provides further spectral information about the sample composition which cannot or not as easily be obtained by common LIBS analysis and is therefore of special interest for e.g. halogens [1,2]. When comparing a standard LIBS experiment with 4 ns pulses to pulses of 550 fs pulse duration, it became apparent that both exhibit molecular band emission. Important factors are plasma temperature and shielding which are both weaker for femtosecond excitation [3]. This benefits the observation of band emission especially in those cases, where the recombining atoms and ions are partly not inherent in the sample. Figure 1 reveals this for CaCl (left) – evolving from a calcium chloride lump – and AlO (right), where a sample of aluminum was used in ambient air. When observing CaCl no gain in information can be achieved since calcium and chlorine are both within the sample and do not need a collapse of the plasma shielding to recombine. Aluminum, on the other hand, can recombine as soon as it can get in contact with the oxygen of the ambient air. We will show a comparison of further different pulse durations from the large nanosecond range to several 100 fs, including the picosecond range.

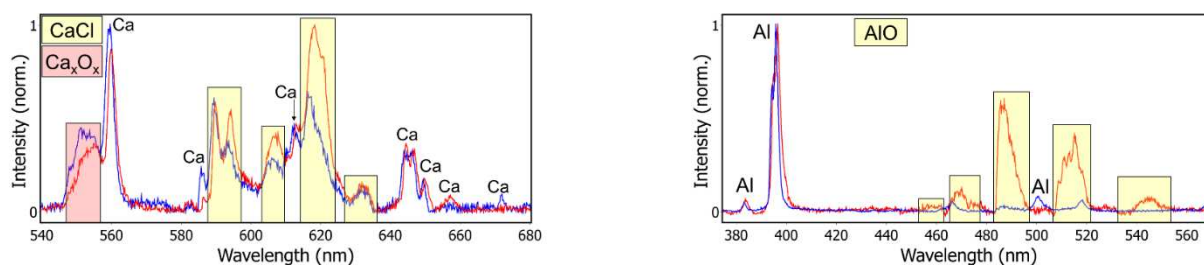


Figure 1: LIBS spectra of calcium chloride (left) and aluminum (right) in ambient air measured without gating. Blue spectra were generated by irradiating nanosecond pulses (4 ns, 1064 nm, 400 mJ/pulse), red spectra by 2000 femtosecond pulses in burst mode (550 fs, 1030 nm, 100  $\mu$ J/pulse). Acknowledgments: We gratefully thank Jenoptik Laser GmbH for providing us the femtosecond laser JenLas® femto 16 for test measurements. References: [1] C. Haisch, R. Niessner, O.I. Matveev, U. Panne, N. Omenetto, "Element-specific determination of chlorine in gases by Laser-Induced-Breakdown-Spectroscopy (LIBS)", *Fresenius J. Anal. Chem.*, 356, 21-26 (1996) [2] A.-S. Rother, T. Dietz, P. Kohns, G. Ankerhold, "Molecular laser-induced breakdown spectroscopy for elemental analysis – A new approach to an advanced material research", *Technisches Messen tm*, vol. 84, no. 1, 23-31 (2017) [3] S. Harilal, J. Yeak, B. Brumfield, M. Phillips, "Consequences of femtosecond laser filament generation conditions in stand-off laser induced breakdown spectroscopy", *Optics Express*, 24(16), 17941-17949 (2016) (DOI: 10.1364/OE.24.017941)

## Design of an online-analysis technique for the determination of major and minor nutrients in soils using double-pulse laser-induced breakdown spectroscopy.

Madlen Rühlmann<sup>\*A</sup>, Thomas Schmid<sup>A</sup>, Markus Ostermann<sup>A</sup>, Dominique Büchele<sup>A</sup>

Federal Institute for Materials Research and Testing (BAM), Richard-Willstätter-Straße 11, 12489 Berlin, Germany.

\*madlen.ruehlmann@bam.de

*ABSTRACT: LIBS (laser-induced breakdown spectroscopy) is known as a fast and simultaneous multi-element analysis with little or no sample preparation. Because of that, over the last few years there has been a growing interest in applications of LIBS in the field of agriculture.*

*As part of the National Research Strategy BioEconomy 2030 the German Federal Ministry of Education and Research (BMBF) started an innovation programme called BonaRes. BonaRes consists of ten interdisciplinary research project associations which are dealing with soil as a sustainable resource for the bio-economy. One of these research projects is I4S (intelligence for soil) which has the goal to develop an integrated system for site-specific soil fertility management. This system includes a sensor platform, which contains different sensors, like XRF, VIS-NIR, Gamma and LIBS. The main task of LIBS measurements in this project is the real time determination of the elemental contents of major and minor nutrients in soils, like calcium, magnesium, potassium. For this purpose, a special setup has been designed. The sample uptake operates with the help of a rotatable sample plate, on which the loose soil sample can be placed in form of a track. The sample plate circulates with different velocities to simulate the application on the field. To provide a higher intensity and a better reproducibility of the obtained signal, a double-pulse Nd:YAG laser ( $\lambda = 1064 \text{ nm}$ ) was used. In order to minimize dust formation from the soil during the operation of the laser, a dust removal by suction has been integrated [1].*

*When using relative methods such as LIBS, a suitable calibration curve is needed for absolute quantification. Within the I4S project a large number of soil samples from different testing grounds with known data of chemical composition, texture etc. is available. For the first calibration curves seven soil samples from different grounds in Germany were prepared as reference materials and four certified reference materials from China and Canada were purchased. With the help of these reference materials, calibration curves for different elements were initially calculated based on internal standard addition. Copper was used as internal standard because of its low concentration in soils. The complex matrix of soils, as well as the influence of moisture and grain size in soils makes the absolute quantification by LIBS challenging. To overcome these influences, a calibration curve based on multivariate analysis was generated. Therefore, baseline correction on the second derivative with a Savitzky-Golay filter was followed by a partial least squares regression (PLSR). Multivariate analysis leads to noise reduction and neglectation of interfering signals. Therefore, a better correlation between signal intensity and nutrient concentration is observed and a robust calibration curve is obtained.*

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## **Determination of Nickel and Cobalt in Food Samples by Using Ultrasound-Assisted Solidified Floating Organic Drop Microextraction Followed by Flame Atomic Absorption Spectrometry**

Çiğdem Arpa Şahin<sup>\*A</sup>, İtir Arıdaşır<sup>A</sup>, İlknur Durukan Temuge<sup>B</sup>, Sema Bektaş<sup>A</sup>

<sup>A</sup>Hacettepe University Chemistry Department, Beytepe, Ankara, Turkey; <sup>B</sup>Hacettepe University Department of Environmental Engineering, Beytepe, Ankara, Turkey

\*carpa@hacettepe.edu.tr

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*ABSTRACT: Nowadays, because of adverse health effects of heavy metals, its determination in natural water and food samples is important for analytical chemistry. But, because of their low concentration and coexistence of matrix species, direct determination of these species in their samples is difficult. So, some methods were developed for preconcentration and separation of analyte before measuring. Separation and preconcentration based on Ultrasound-assisted solidified floating organic drop microextraction (USA-SFODME) is becoming an important and practical A simple, rapid, inexpensive, and nonpolluting USA-SFODME technique has been improved for the preconcentration and determination of nickel and cobalt in food samples. For this purpose Congo Red (CR) was used as a complexing agent and 1-dodecanol was used as an extraction solvent. Several factors affecting the microextraction efficiency, such as, pH, CR and concentration, extraction time, and temperature were investigated and optimized. The developed method was applied to the determination of trace nickel and cobalt in water and food samples with satisfactory results.*

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## Influence of the Spot Size on ZnO Thin Films Produced by Pulsed Laser Deposition

A. Yáñez-Guzmán<sup>A</sup>, A. Fernández<sup>A</sup>, C. Sánchez Aké<sup>\*A</sup>, T. García-Fernández<sup>B</sup>, M. Villagrán-Muniz<sup>A</sup>

<sup>A</sup>Laboratorio de Fotofísica, Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México, Apartado Postal 70-186, Cd. Mx., C.P. 04510, México; <sup>B</sup>Universidad Autónoma de la Ciudad de México (UACM), Prolongación San Isidro 151, San Lorenzo Tezonco, Cd.Mx, C.P. 09790, México.

\*citlali.sanchez@ccadet.unam.mx

**ABSTRACT:** It is well known that the characteristics of thin films produced by pulsed laser deposition (PLD) depends on the properties of the ablation plume since it provides the material flux for film growth<sup>[1]</sup>. For this reason, there are several works of PLD that study the effect of the deposition conditions on the thin films. However, an important number of papers report only the laser fluence employed for deposition without specifying the laser beam spot size and beam energy. In particular, the laser beam spot size affects the dynamics of the plume expansion<sup>[2]</sup> and the ablation rate<sup>[3]</sup>, therefore this parameter can change the characteristics of the deposited film. To investigate this effect, we deposited ZnO thin films by laser ablation and employed time-resolved optical emission spectroscopy to study the expansion of the plasma plume produced with various spot sizes. All experiments were performed in the presence of O<sub>2</sub> gas, using ns laser pulses at a fixed fluence of 2 J/cm<sup>2</sup>. The temporal evolution of the electron density and temperature was determined as a function of the distance along the normal direction to the target surface. The composition, crystalline structure and optical properties of the films were compared with the plasma parameters. Our results demonstrate that the composition of the films, the thickness of the films and their transparency strongly depend on the spot size of the laser beam even for a fixed laser fluence.

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## Removing interferences in organic solvents and petroleum products by hTISIS-ICP-MS/MS

Carlos Sánchez<sup>\*A,B</sup>, Fabien Chainet<sup>B</sup>, Charles Philippe Lienemann<sup>B</sup>, José Luis Todolí<sup>A</sup>

<sup>A</sup>Department of Analytical Chemistry, Nutrition and Food Sciences, University of Alicante, Alicante, Spain;

<sup>B</sup>Physics and Analysis division, IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP3, 69360, Solaize, France.

\*carlos.sr@ua.es

**ABSTRACT:** Petroleum products and organic solvents can contain metals and metalloids. They can be present under different chemical forms in crude oil or they can be incorporated to the final product during refining process. The presence of these compounds in fuel can cause damages in engines that use them, environmental pollution and health problems. On the other hand, if they are present in crude oil, they can act as catalyst poison, even at low concentrations. For these reasons, since the presence of metals in petroleum was established in 1935<sup>1</sup>, some studies have been focused on the development of analytical methods based on ICP (inductively coupled plasma) techniques to carry out the determination of metals and metalloids in this kind of samples. However, several difficulties have been observed: (i) the concentration of some metals in fossil fuels and organic solvents is in the order of ng g<sup>-1</sup>; (ii) the organic matrices can cause the plasma degradation; (iii) the complexity of the matrices and their differences in terms of physical properties causes significant matrix effects.

To overcome these problems, several sample introduction systems have been developed as cold spray chambers or desolvation systems<sup>2</sup>, which can mitigate matrix effects. However, they are not able to completely remove the matrix effects between different fossil fuels and organic solvents. In these new introduction systems is also included the total sample consumption system called hTISIS (high temperature Torch Integrated Sample Introduction System), which has been employed successfully to achieve the removal of matrix effects for different organic solvents and fossil fuels.<sup>3</sup> Moreover, when this system was coupled to ICP-MS, polyatomic interferences disturbed the spectra due to the massive presence of carbon and oxygen within the plasma causing the degradation of the limits of detection for some interfered isotopes as <sup>28</sup>Si<sup>+</sup> (<sup>12</sup>C<sup>16</sup>O<sup>+</sup>, <sup>14</sup>N<sub>2</sub><sup>+</sup>), <sup>32</sup>S<sup>+</sup> (<sup>16</sup>O<sub>2</sub><sup>+</sup>), <sup>40</sup>Ca<sup>+</sup> (<sup>40</sup>Ar<sup>+</sup>), <sup>52</sup>Cr<sup>+</sup> (<sup>40</sup>Ar<sup>12</sup>C<sup>+</sup>), <sup>56</sup>Fe<sup>+</sup> (<sup>40</sup>Ar<sup>16</sup>O<sup>+</sup>) or <sup>75</sup>As<sup>+</sup> (<sup>40</sup>Ar<sup>35</sup>Cl<sup>+</sup>).

In the present work, the hTISIS was coupled to an ICP-MS/MS Agilent 8800 to develop an analytical methodology to carry out the determination of trace metals strongly interfered in petroleum products and organic solvents. On the one hand, the use of the hTISIS at 350°C overcomes the matrix effects between the different matrices studied and it allows the external calibration using standards prepared in pure xylene. Additionally, the ICP-MS/MS using O<sub>2</sub> or/and H<sub>2</sub> as reaction gases overcomes the isobaric interferences observed in an ICP-MS equipped with a single quadrupole. Non-spiked and spiked real fuels were analyzed providing acceptable recoveries. The proposed methodology solves the main problem related to the quantification of metals and metalloids in organic samples without causing the degradation of the analytical figures of merit.

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## Assessing the efficacy of the EDXRF/Monte Carlo Simulations approach in the analysis of ancient metal artifacts: an experimental study on artificial corroded alloy samples

Nick Schiavon<sup>\*A</sup>, Emma Angelini<sup>B</sup>, Sabrina Grassini<sup>A</sup>, Antonio Brunetti<sup>C</sup>

<sup>A</sup>Hercules Laboratory, University of Évora, Largo Marquês de Marialva 8, Évora, Portugal; <sup>B</sup> Department of Applied Science and Technology, Corso Duca degli Abruzzi 24, Turin Polytechnic, Turin, Italy; <sup>C</sup>POLCOMING Department, University of Sassari

\*schiavon@uevora.pt

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*ABSTRACT: Recent studies on the application of a combined totally non destructive EDXRF/Monte Carlo simulations analytical approach to obtain the quantitative elemental composition of the original alloy substrate in ancient bronze artifacts without the need to remove the surface corrosion patinas, while proving the potentiality of the method, have also highlighted the need to importance of the compositional heterogeneity of the bronze and patinas as well as the varying thickness of the superficial corrosion patinas in the quality of the Monte Carlo simulation runs[1-3]. To test the efficacy of the combined EDXRF/Monte Carlo methodological approach, the same protocol has been applied in the current study to bronze alloy samples artificially corroded in controlled laboratory conditions with patinas of known composition and thickness. Preliminary results show a good fit between the real and Monte Carlo simulated spectra, thus confirming the applicability of the protocol to archaeological and cultural heritage artifacts .*

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## Iodine determination by high resolution continuum source molecular absorption spectrometry: A comparative between promising molecules.

Mauana Schneider<sup>A</sup>, Mao-Dong Huang<sup>B</sup>, Helmut Becker-Ross<sup>B</sup>, Bernhard Welz<sup>A,C</sup>

<sup>A</sup>Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis, Brazil; <sup>B</sup>ISAS – Leibnitz Institute for Analytical Sciences, Berlin, Germany, <sup>C</sup>Instituto Nacional de Ciência e Tecnologia do CNPq, INCT de Energia e Ambiente, Universidade Federal da Bahia, Salvador, BA, Brazil.

mauana.schneider@gmail.com

**ABSTRACT:** The direct determination of halogens by conventional atomic absorption spectrometry is not possible, once their resonance lines are below 190 nm in the vacuum-UV. An alternative for the atomic resonance lines is the indirect determination via diatomic molecules composed by the halogen and a molecule-forming reagent. The gaseous diatomic molecules are able to absorb radiation in the ultraviolet and visible wavelength range and like the absorbance of atoms, that of diatomic molecules also obeys Lambert-Beer's law. In the 1980s and 1990s some workers proposed the use of line-source atomic absorption spectrometers for the determination of halogens, using wavelengths, emitted by a line source that accidentally coincided with a molecular absorption band; however this practice was susceptible to interferences since the spectral neighborhood was unknown and the available background correction systems failed. Thus, the low-resolution monochromator of line-source atomic absorption spectrometers cannot separate correctly the fine structure of the molecular bands. With the advent of high-resolution continuum source atomic absorption spectrometry, the determination of halogens via diatomic molecular spectra became possible due to the high-resolution monochromator system, providing a better split of the wavelengths, a high intensity xenon arc lamp emitting a continuum between 190 nm and 890 nm, and a CCD array detector, which permits a three-dimensional view of the spectra and the spectral neighborhood. These features made the determination of halogens possible with low limits of detection when compared with electrochemical or classic methods. Several papers have been published describing the determination of fluorine, chlorine and bromine, using a series of metals as reagents, which are able to form a diatomic molecule with the halogen at high temperatures provided by the electrothermal vaporization. However, there is a lack of publications about iodine determination by HR-CS GF-MAS; the reason is the low dissociation energy of the diatomic molecules formed with iodine, less than 500 kJ mol<sup>-1</sup>, which turns the molecule unstable at high temperatures and, in the presence of other halogens, the competition for the molecule-forming reagents results in low sensitivity and interferences. Some diatomic molecules of iodine presented a good thermal stability, even with dissociation energy lower than 500 kJ mol<sup>-1</sup>, when submitted to an optimized temperature program, such as BaI, which exhibits high sensitivity when pyrolysis temperatures up to 600 °C and a vaporization temperature of 2000 °C were applied in a graphite tube without permanent modifier [1]. Calcium can also be used as molecule-forming agent and, with an optimized temperature program of 1500 °C pyrolysis and 2500 °C vaporization temperature, using an iridium-coated tube, produces a highly sensitive band. This work presents a comparison between CaI, BaI, SrI and YI molecules, studying their characteristic mass, thermal stability, permanent modifiers, possible interferences, more sensitive wavelengths and possibilities of applications.[1] M.D. Huang, H. Becker-Ross, S. Florek, M. Okruss, B. Welz, S. Morés, Spectrochim. Acta Part B 64 (2009) 697.

## Quantification of Chlorine via Molecular Emissions of CaCl in Laser-induced Breakdown Spectroscopy under Martian Conditions

David S. Vogt<sup>\*A</sup>, Kristin Rammelkamp<sup>A</sup>, Susanne Schröder<sup>A,B</sup>, Heinz-Wilhelm Hübers<sup>A,C</sup>

<sup>A</sup>Institute of Optical Sensor Systems, Deutsches Zentrum für Luft- und Raumfahrt (DLR), Berlin, Germany;

<sup>B</sup>Institut de Recherche en Astrophysique et Planétologie (IRAP), Toulouse, France; <sup>C</sup>Department of Physics, Humboldt-Universität zu Berlin, Berlin, Germany.

\*david.vogt@dlr.de

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**ABSTRACT:** The ChemCam instrument suite on board the Mars Science Laboratory and its successor, SuperCam, use laser-induced breakdown spectroscopy (LIBS) at stand-off distances for the elemental analysis of Martian targets [1–3]. The detection of halogens like chlorine in Martian targets has been a challenge for ChemCam, as the emission lines are typically of low intensity, so that high concentrations are necessary. An indirect detection via molecular emissions of simple molecules that form inside the plasma has been proposed as a way to enhance the level of detection (LOD) for halogens [4]. In the case of chlorine, the molecular emissions of calcium monochloride (CaCl) have been useful for the identification of chlorine in ChemCam spectra [5]. Its strongest bands, located at 593 nm and 618 nm in the spectra, lie within ChemCam's spectral range. The LOD for chlorine can significantly improve when using CaCl bands instead of atomic emission lines [6]. However, the dependency on compositional changes of the samples has not yet been investigated extensively. Since the formation of a diatomic molecule is a prerequisite for these molecular emissions, the concentrations of both elements inside the laser-induced plasma are likely to have a big influence on the intensity of the molecular bands. This study investigates these effects under Martian conditions. Samples were created with compositions that resemble Martian targets, and were measured in 6.5 mbar of Mars-analog atmosphere. The reactions inside the plasma are modeled in order to investigate the changes in CaCl concentration over time. The concentration of Ca is found as a strong limiting factor for the band intensity. Since time-resolved LIBS measurements on Mars will be possible for the first time with SuperCam, the optimization of the delay time for measurements of CaCl bands on Mars will also be discussed.

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## Micro-Laser Induced Breakdown Spectroscopy for recognition of chemical zoning of Ti-rich garnets in thin section.

Giovanna Agrosi<sup>A</sup>, Paola Manzari<sup>B</sup>, Giorgio S. Senesi<sup>C\*</sup>, Gioacchino Tempesta<sup>A</sup>

<sup>A</sup> Dipartimento di Scienze della Terra e Geoambientali (DiSTeGeo), University of Bari, Via E. Orabona 4, 70125 Bari, Italy; <sup>B</sup> Istituto Nazionale di Astrofisica - Istituto di Astrofisica e Planetologia Spaziali (INAF-IAPS), via Fosso del Cavaliere 100, Roma, Italy; <sup>C</sup> CNR, Istituto di Nanotecnologia (NANOTEC) - PLasMI Lab Lab, Via Amendola 122/D, 70126 Bari, Italy

\* giorgio.senesi@nanotec.cnr.it

**ABSTRACT:** Ti-rich garnets are minerals related to alkali metasomatism and magmatism of carbonatic affinity, which can be found in various undersaturated alkaline igneous rocks. The chemical composition of these minerals depends on the physico-chemical growth conditions under which they formed. Thin sections of these garnets often exhibit colour zonings corresponding to chemical zonings. The innovative approach of double-pulse micro-laser-induced breakdown spectroscopy (DP- $\mu$ LIBS) technique coupled with optical microscopy can be fruitfully applied to the direct quantitative analysis and characterization in atmospheric air of the petrographic thin sections [1]. This method shows significant advantages with respect to traditional techniques used to analyze geological samples such as electron-probe microanalysis (EPMA) and scanning electron microscopy-energy dispersive spectrometry (SEM-EDS), including versatility, minimal destructivity, no carbon coating, no waste production, low operating costs, rapidity of analysis and sensitivity to light elements. To validate the analytical performance of this technique, several petrographic thin sections of Ti-rich andradite garnets originated from the volcanic district of Colli Albani, Italy, were investigated. Some of these petrographic thin sections have been previously investigated by EPMA [2-4], and the analyses obtained were used to set-up the one point calibration (OPC) LIBS method in order to determine quantitatively the chemical composition of Ti-rich garnets. This method was then applied also to thin sections of garnet not previously investigated by conventional techniques. Several analytical spots were aligned along different directions on the slices. The results obtained show that the samples studied exhibit two different types of chemical zonings. A decrease of Ti content from core to rim of slices, which reflects the physico-chemical evolution of the growth environment (concentric zoning), and an increase of Ti in the {211} growth sectors, related to growth kinetics [3] (sector zoning). The OPC-LIBS data show a good agreement with the previous EPMA data, suggesting that the DP- $\mu$ LIBS can be considered a good tool to obtain quick, fast and reliable chemical analyses of petrographic thin sections.

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## Characterization of Signal Variation by Metal Types and Surface Conditions during Laser Induced Breakdown Spectroscopy.

Sungho Shin, Hyemin Jang, Jaepil Lee, Jang-Hee Choi, Euseok Hwang, Sungho Jeong\*

School of Mechanical Engineering, Gwangju Institute of Science and Technology, 1 Oryong-dong Buk-gu  
Gwangju 500-712, Republic of Korea.

\* shjeong@gist.ac.kr

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*ABSTRACT: Recently, sorting of scrap metals by laser induced breakdown spectroscopy (LIBS) has been reported by several researchers, which is mainly based on the capability of fast measurement of LIBS. For the successful implement of a LIBS-based metal sorting system, it is critical to be able to accurately identify different types of scrap metal regardless of its surface conditions. A scrap metal is typically in poor conditions such that the surface is rusted, painted, and/or contaminated by dust and lubricant. Also, scrap metals often undergo a shredding process, which leaves a rough and irregular surface. Therefore, the LIBS signal of scrap metals can change significantly between pulses and samples even if the bulk material is the same. In this work, the influence of surface conditions on the LIBS signal changes is investigated. The variation of LIBS signal intensities depending on surface conditions is analyzed using real scrap samples collected from a recycling company and compared with those of certified reference material. The signal dependence on surface conditions is characterized for the determination of proper emission lines for more accurate sorting and a classification algorithm considering these changes is developed.*

### Acknowledgement:

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## Optimization of measurement technique for automated DGM determination in water

Sergey Sholupov<sup>\*A</sup>, Nikolay Mashyanov<sup>B</sup>, Sergey Pogarev<sup>B</sup>, Vladimir Ryzhov<sup>C</sup>, Francesco Fornai<sup>D</sup>,  
Francesco Bartaloni<sup>D</sup>, Giacomo Saviozzi<sup>D</sup>, Cecilia Laschi<sup>D</sup>, Paolo Dario<sup>D</sup>, Francesco Pacini<sup>E</sup>,  
Giancarlo Teti<sup>F</sup>, Luca Volpi<sup>F</sup>

<sup>A</sup>Lumex-marketing LLC, St. Petersburg, Russia, <sup>B</sup>St. Petersburg State University, St. Petersburg, Russia, <sup>C</sup>Lumex Analytics GmbH, Wakendorf, Germany, <sup>D</sup>The BioRobotics Institute, Scuola Superiore Sant'Anna, (SSSA), Pisa, Italy, <sup>E</sup>Whitehead Sistemi Subacquei S.p.A. (WASS Finmeccanica), Livorno, Italy, <sup>F</sup>RoboTech Srl, San Piero a Grado (Pisa), Italy

\*SholupovSE@lumex.ru

**ABSTRACT:** Mercury in surface water partially occurs in a form of dissolved atomic vapor, so called DGM (Dissolved Gaseous Mercury). DGM represents a considerable proportion of total Hg (THg) up to 25 % of THg. Volatile DGM plays an important role in the mercury transfer through the water-air interface. A newly developed automated DGM monitor consists of a reaction vessel (Italian patent, worked out at SSSA) based on the opposite flow principle and a mercury analyzer. The DGM monitor integrated with an underwater piston sampling system has been mounted on board of a compact V-FIDES Autonomous Underwater Vehicle (AUV) equipped with a multi-parametric probe measuring sea water parameters (pH, salinity, oxygen, etc.). Specific feature of the AUV is its very small internal space and, consequently, a very small volume (0.2 – 1 L) of a water sample to be delivered to the reaction vessel. For the system parameters optimization (water and gas flows, sample volume, measurement procedure) as well as to define the memory effects, a real time Zeeman mercury analyzer RA-915+ (Lumex) was used. The analyzer continuously measures the Hg concentration with averaging time of 1 s and the detection limit of 1 ng/m<sup>3</sup>. Principle of operation of RA-915+ is as follows. A mercury discharge lamp is placed in a strong magnetic field, whereby the Hg emission resonance line at 254 nm is split into the three polarized Zeeman components  $\sigma_-$ ,  $\pi$ , and  $\sigma_+$ . Only the  $\sigma$ -components are registered by the photodetector. The  $\sigma_-$ -component is located in the vicinity of the maximum of the absorption mercury line and plays a role of an analytical line, while  $\sigma_+$ -component lies outside the resonance absorption line and is used as a reference line. The  $\sigma_-$  and  $\sigma_+$  – components are separated by a polarization modulator. When mercury atoms are absent in the cell, the intensities of both  $\sigma$ -components are equal. When mercury occurs in the cell, the difference in the intensities between the two  $\sigma$ -components increases as a function of the mercury concentration. The use of the differential atomic absorption spectrometry with the direct Zeeman effect enables the detection limit to be significantly reduced because of elimination of flicker noise and increase in sensitivity by using a multipath cell. The low detection limit allows one to avoid preliminary Hg accumulation on sorbent traps and to obtain real-time data, which is very important at the stage of building the analytical system. The DGM extraction efficiency was studied using a water solution of elemental mercury. A small amount (0.5 g) of metal mercury was placed in a bottle with 1 L of distilled water. The mercury concentration in the water increased steadily and stabilized in 5-7 days at a level of 30 - 50 ug/l. The water solution of DGM was used for optimization of the reaction vessel parameters and for system calibration. As a result, a compact device was developed for the fully automatic measurement of DGM concentrations in deep waters without accumulation of Hg on a sorbent. An original technique for calibration and optimization of the parameters of DGM solutions at very low concentrations has been proposed and validated. The V-FIDES project is cofounded by the Tuscany Region (Italy) in the FAR PAS programme.

## Real-time highly sensitive and selective benzene and mercury determination in air and natural gas by differential absorption spectrometry with the direct Zeeman effect

Sergey Sholupov <sup>\*A</sup>, Alexander Ganeev <sup>A</sup>, Sergey Pogarev <sup>B</sup>, Vladimir Ryzhov <sup>C</sup>

<sup>A</sup>Lumex-marketing LLC, St. Petersburg, Russia, <sup>B</sup>St. Petersburg State University, St. Petersburg, Russia, <sup>C</sup>Lumex Analytics GmbH, Wakendorf, Germany.

\*SholupovSE@lumex.ru

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**ABSTRACT:** A new technique is proposed for the real-time determination of benzene and mercury vapor in the atmospheric air and natural gas by absorption spectrometry with the direct Zeeman effect. Resonance mercury emission at a wavelength of 254 nm is used as the probing radiation. The wavelength dependences of the differential absorption cross sections of benzene and mercury are determined by magnetic scanning technique using mercury lamps with different isotopic compositions. The use of a lamp with the mercury isotope <sup>204</sup>Hg made it possible to enhance sensitivity four-fold for benzene and mercury as compared to a lamp with the natural isotopic mixture. It is experimentally demonstrated that the interference from SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>3</sub> can be neglected for determination of benzene (at the Occupational Exposure Limit (OEL)) and mercury (at background level) if the concentrations of these gases do not exceed the corresponding OELs. Basing on the results of our study, a portable spectrometer is designed with the detection limit of 0.5 mg/m<sup>3</sup> for benzene and 2 ng/m<sup>3</sup> for mercury (benzene concentration being below OEL) at 1-s averaging. To measure the benzene and mercury concentrations separately, two gas channels are used wherein filters with different transmission of benzene and mercury are inserted. The applications of the designed spectrometer to measuring the benzene and mercury concentrations in the atmospheric air from a moving vehicle and in natural gas are exemplified.

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## Substrate effect on the LIBS emission of nanometer scale thick layers

Panayiotis Siozos<sup>\*A</sup>, Shyama Prasad Banerjee<sup>B</sup>, Nikos Giannakaris<sup>C</sup>, Thierry Sarnet<sup>B</sup>, Dimitrios Konios<sup>D</sup>, Miron Krassas<sup>D</sup>, Emmanuel Stratakis<sup>A</sup>, Emmanuel Kymakis<sup>D</sup>, Marc Sentis<sup>B</sup>, Demetrios Anglos<sup>A,C</sup>

<sup>A</sup>Institute of Electronic Structure and Laser (IESL), FORTH, 71110, Heraklion, Crete, Greece;

<sup>B</sup>Laboratoire LP3, Case 917, 163 Avenue de Luminy, Marseille, 13009, France;

<sup>C</sup>Department of Chemistry, University of Crete, 71003 Heraklion, Crete, Greece;

<sup>D</sup>Center of Materials Technology and Photonics & Electrical Engineering Department, School of Applied Technology, Technological Educational Institute (TEI) of Crete, 71004, Heraklion, Crete, Greece;

\*psiozos@iesl.forth.gr

**ABSTRACT:** Material distribution or compositional analysis and depth profiling of nanometer thick multi-layered samples require the use of sophisticated techniques. Laser Induced Breakdown Spectroscopy (LIBS) has been demonstrated for selective detection of materials at different depths from nanometer scale multilayered samples [1]. Due to the simplicity of the method LIBS can be applied for rapid characterization of the ultra-thin nanometer layers which is of significant importance in particular for industrial applications, such as semiconductors and photovoltaics production monitoring. The processes that take place during emission from a very thin layer are very complex and therefore extent research must be carried. In the present work the different characteristics of the LIBS emission recorded from nanometer scale thick layers of the same material deposited on the top of two different types of samples, were studied. We have carried out LIBS measurements using a 50 picosecond laser source at two different wavelengths (1030 and 515 nm) with very low pulse energy (<10  $\mu$ J/pulse) and a Czerny-Turner spectrometer (600 lines/mm) coupled with an ICCD (Andor iStar DH734.) for spectral detection of the laser induced plasma. Two types of samples were used: a) Indium Tin Oxide layer (125 nm), SiN layer (150 nm) on PET substrate and b) Indium Tin Oxide (60 nm) layer on glass substrate. In the first sample clear indium emission (410.176 nm) that represents the ITO layer, were recorded on the first laser pulse at 1030 nm wavelength. In the second sample indium emission was also detected in the first pulse using the 1030 nm wavelength but indium lines were absent in the spectra in the case of 515 nm laser pulses. This observation points out the influence of the laser parameters, subjacent layers and the substrates in the formation of the LIBS emission. Finally, the LIBS emission from a ~300 nm PEDOT-PSS layer on top of a glass substrate was recorded under the same experimental conditions. The presence of clear C-N molecular band emission at 388.2 nm using the 1030 nm laser pulse was detected in the second pulse, demonstrating the potential of LIBS for selective detection of organic materials in nanometer scale layers, using the C-N molecular emission. This project is under the support of the International Associated Laboratory (LIA) MINOS between LP3 and IESL-FORTH. [1] S.P. Banerjee, T. Sarnet, P. Siozos, M. Loulakis, D. Anglos, M. Sentis, Appl. Surf. Sci. 2016, in press; doi: 10.1016/j.apsusc.2016.11.136



## Micro-laser induced breakdown spectroscopy of an iron meteorite

Tempesta, G.\*<sup>A</sup>, Manzari, P.<sup>B</sup>, Senesi, G.S.<sup>C</sup> and Agrosi, G.<sup>A</sup>

<sup>A</sup> Dipartimento di Scienze della Terra e Geoambientali (DiSTeGeo), University of Bari, Via E. Orabona 4, 70125 Bari, Italy

<sup>B</sup> Istituto Nazionale di Astrofisica - Istituto di Astrofisica e Planetologia Spaziali (INAF-IAPS), via Fosso del Cavaliere 100, Roma, Italy

<sup>C</sup> CNR – Istituto di Nanotecnologia (NANOTEC) – PLasMI Lab, Via Amendola 122/D, 70126 Bari, Italy

\*gioacchino.tempesta@uniba.it

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**ABSTRACT:** The study has been conducted on two samples of the iron meteorite Dronino in the framework of a campaign aiming to validate planetary data on terrestrial and extra-terrestrial materials by portable techniques. The samples were studied by a portable double-pulse micro-laser-induced breakdown spectroscopy (DP- $\mu$ LIBS) system coupled with optical microscopy [1]. The two fragments of Dronino have very different features, i.e. one sample is highly altered, while the other one does not show any superficial alteration but has sulphide inclusions rounded and elongated along the banding. According to the Meteoritical Bulletin Database (MBD) Dronino meteorite belongs to an ungrouped ataxite meteorites and consists of kamacite ( $7.0 \pm 0.5$  wt% Ni and 0.75 wt% Co) and rare taenite ( $26.5 \pm 0.5$  wt% Ni and 0.35 wt% Co). The altered sample has been found in a swamp and suffered of marked weathering effects that modified the mineralogy and chemistry of the whole sample. The quantitative chemical composition measured by DP- $\mu$ LIBS with One Point Calibration method [2] showed that the two samples were very different. The scanning electron microscopy (SEM) EDS analyses confirmed the DP- $\mu$ LIBS results and showed that the unaltered slab consisted mainly of taenite (26.6 wt% Ni and 0.6 wt% Co), whereas kamacite (8.2 wt% Ni and 1.1 wt% Co) was present in only one point. Differently, the altered sample consisted mainly of kamacite (6.2 wt% Ni and 1.02 wt% Co), as described in the MBD. The differences found between DP- $\mu$ LIBS data and SEM results were ascribed to the heterogeneity of the sample and to the different sampling areas. In fact, the SEM chemical map showed a very fine grade texture of elongated precipitates (duplex structure) in the unaltered sample. In the altered sample DP- $\mu$ LIBS indicated the presence of a Li peak on several spots, whereas Li was absent in the unaltered sample. In particular, Li is a light trace element not detectable by routinely techniques such as SEM EDS or X-ray fluorescence. The importance to evaluate Li both qualitatively and quantitatively has been already highlighted by previous studies made by ChemCam LIBS analysis on the Martian surface [3-4]. In fact, this element can provide evidence of alteration processes that might have affected extra-terrestrial rocks, i.e. the presence of Li in the meteorite sample would be related to the weathering processes due to aqueous solutions occurred in the swamp. [1] Senesi et al., 2016, *Geostandards and Geoanalytical*, Volume 40, Issue 4, Pages 533–541 [2] Cavalcanti G.H., Teixeira D.V., Legnaioli S., Lorenzetti G., Pardini L., Palleschi V., 2013, *One point calibration for calibration-free laser-induced breakdown spectroscopy quantitative analysis*, *Spectrochim. Acta Part B*, 87, 2013, 51–56. [3] Maurice et al., 2016, *Journal of Analytical Atomic Spectrometry* Volume 31 Number 4, Pages 823–1050 [4] Ollila et al., 2014, *JGR-Planets*, Volume 119, Issue 1, Pages 255–285

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## Determination of Lead in Flour Directly by Solid Sampling High Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry

Hande Tınas<sup>A</sup>, Nil Ozbek<sup>A</sup>, Suleyman Akman<sup>A</sup>

<sup>A</sup> Department of Chemistry, Istanbul Technical University, Maslak, Istanbul, Turkey.

\*tinash@itu.edu.tr

**ABSTRACT:** Flour is a main ingredient of the most commonly and highly consumed foods such as bread, macarroni, pastry, cake dessert, pita, pizza etc. Therefore, its toxic element contents is highly important for human health. Flour may be polluted in every stage of its production during growing from soil, air and water, harvesting, storage, grinding, packing etc. In addition, different crops e.g. wheat, rice, corn, maize intake the elements at different amounts during growing even at the same environmental conditions. The lead of flour can be determined by atomic absorption spectrometry or other techniques after acid digestion. However, digestion is highly time consuming, prone to analyte loss and contamination. In addition, the acids and other chemicals used for digestion may cause irreproducible blank values and contribute to environmental pollution and detrimental effects for human health. Solid sampling is basically based on the direct introduction of sample without any treatment. Analytical procedure is very simple. After the experimental conditions and instrumental parameters are optimized, if necessary, the sample is grinded, put on the sampler and measured. It is environmentally-friendly since harmful chemicals (acids etc.) are not used. Blank values are low. Dilution errors were eliminated. It is relatively cheaper because expensive ultra-pure chemicals and laboratory equipment such as microwave-assisted digestion systems are not needed. The contamination and analyte loss during sample preparation do not occur. Therefore, the drawbacks and risks in digestion and slurry techniques are eliminated. Solid sampling has been successfully used for the determination of several elements in various samples. It is the most powerful technique due to advantages over other sampling techniques. In this study, lead was determined without digesting flour samples, by high-resolution continuum source graphite furnace atomic absorption spectrometry with solid sampling. Since samples were directly analyzed, the risks and disadvantages occurred during sample preparation were eliminated. For flour samples, even grinding was not needed as well. Solid samples were only dried, weighed on the platforms, Pd was added as a modifier and introduced to a Zr-coated furnace using a manual solid sampler. The optimized pyrolysis/atomization temperatures were 900/2200 °C. The sensitivities of various flour CRMs and aqueous standards were not significantly different. Therefore, aqueous standards were safely used for calibration. The LODs and characteristic masses for lead were 0.007 ng g<sup>-1</sup> and 15 pg, respectively. The lead concentrations in flour varieties were determined applying the optimized conditions. The repeatability of the results was relatively low (RSD was 15 to 20%) which is however the case for solid sampling due to heterogeneity of the analyte in micro-scale. Finally, owing to the small sample quantities used for analysis, the micro-scale distribution of analytes in flour samples were determined.

## Simple PXRF Field Measurement Methodology for Trace Elements in Soil

Ricardo Urrutia-Goyes<sup>\*A</sup>, Ariadne Argyraki<sup>B</sup>, Nancy Ornelas-Soto<sup>C</sup>

<sup>A</sup>Universidad de las Fuerzas Armadas ESPE, Sangolqui, Ecuador; <sup>B</sup>Faculty of Geology and Geoenvironment, National and Kapodistrian University of Athens, Athens, Greece; <sup>C</sup>Laboratorio de Nanotecnología Ambiental, Tecnológico de Monterrey, Monterrey, México.

\*erurrutia@espe.edu.ec

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*ABSTRACT: Sites around the world have been reported to be polluted with different trace metals. Prompt monitoring for consequent remediation can be achieved by applying innovative field and analytical techniques. The use of portable x-ray fluorescence (PXRF) in the characterization of soils and other media has been performed in the last decade and improvements in portability, price and accuracy have made these devices to be used more broadly for environmental purposes. In order to measure trace metal concentrations in soil using PXRF, it is recommended that samples taken should be disaggregated, sieved and ground; and that the nose of the device should be placed on top of a sample covered by a thin-film. Given the challenging conditions found in the field, this study was focused on testing the limit of tolerance of these recommendations in order to determine how much a measurement set-up can differ and preserve usable readings. Decreasing particle size of the samples, different distances from the device to the samples, and polypropylene bags of various thicknesses were used in alternate set-ups to compare and contrast outcomes. The minimum reliable characteristics were defined for a simple measurement methodology. Results show that: (1) commercial polypropylene bags of 50 or 100  $\mu\text{m}$ , will allow for a confidence in the readings of 95 and 90% respectively compared to using thin-films; (2) sieving the sample to a maximum particle size of 420, 297, and 252  $\mu\text{m}$  will allow for a confidence in the readings of 80, 85, and 90% respectively compared to grinding the sample after sieving to 149  $\mu\text{m}$ ; and (3) a separation of up to 1.89 mm will lead to a 95% confidence in the readings compared to the device touching the sample. This study can serve as a guide for field workers in order to keep track of the expected accuracy of the technique and to preserve it as reliable alternative in environmental studies.*

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## Determination of Chromium and Cadmium in Mushroom Samples by HR-CS SS-GF AAS

Josi G. César<sup>A</sup>, Ariane V. Zmozinski<sup>B</sup>, Wiliam Boschetti<sup>C,D</sup>, Maria Goreti R. Vale<sup>\*A,C,D</sup>

<sup>A</sup>Instituto de Ciência e Tecnologia de Alimentos, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, Brazil; <sup>B</sup>Escola de Engenharia, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, Brazil; <sup>C</sup>Instituto de Química, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, Brasil; <sup>D</sup>Instituto Nacional de Ciência e Tecnologia de Energia e Ambiente, Universidade Federal da Bahia, Salvador, BA, Brazil.

\*mgrvale@ufrgs.br

**ABSTRACT:** Mushrooms have a high nutritional value, but they also have capacity to accumulate potentially toxic metals. Thus, suitable analytical techniques are required for determination of these metals. In this study, the feasibility of Cr and Cd determination in mushroom samples using direct solid sample analysis and high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS SS-GF AAS) was investigated. Were development two methods, one for Cd and one for Cr. The measurements were performed using a high-resolution continuum source atomic absorption spectrometer Model contraAA 700. The equipment is equipped with a transversely heated graphite tube atomizer. The analytical lines used were 359.348 nm (Cr) and 228.801 nm (Cd). The samples were weighed directly onto the platform and introduced into the graphite tube using a pre-adjusted pair of tweezers for the determination of Cr (0.01 - 0.2 mg) and Cd (0.01 - 0.3 mg). Six samples of mushrooms were analyzed after grinding in a vibratory mill and sieving through a polyester mesh of 77 µm. Pyrolysis temperatures of 1600 °C (Cr) and 800 °C (Cd) and atomization temperatures of 2500 °C (Cr) and 1600 °C (Cd) were used. The addition of a chemical modifier 0.05% Pd(NO<sub>3</sub>)<sub>2</sub> + 0.03% Mg(NO<sub>3</sub>)<sub>2</sub> + 0.03% Triton X-100 was required only for Cd. The calibration could be carried out using aqueous standards. The precision of the methods was verified by the relative standard deviation (n= 5) for the six samples which was lower than 10%. The figures of merit were: LOD of 23 µg kg<sup>-1</sup> and a m<sub>o</sub> of 2.5 pg for Cr; LOD of 0.80 µg kg<sup>-1</sup> and a m<sub>o</sub> of 0.40 pg for Cd. To verify the accuracy of the proposed methods, two certified reference materials were analysed: Virginia Tobacco Leaves CTA-VTL-2 (Cr) and Spinach leaves 1570<sup>a</sup> (Cd). The results found in this work are in agreement with certified values at a 95% confidence level (Student's t-test). The concentrations range found in the mushroom samples were 197-4414 µg kg<sup>-1</sup> for Cr and 18-586 µg kg<sup>-1</sup> for Cd. According to the Brazilian resolution RDC n° 269/2005, one mushroom sample (*B. luteus*) would reach the recommended concentration for Cr (35 µg dia<sup>-1</sup>) if its consumption 10 g per day. In the case of Cd, two samples (*Pleurotus spp.* and *Lentinus spp.*) showed concentrations lower than stipulated by the ANVISA resolution RDC n° 42/2013 (50 µg kg<sup>-1</sup>). The developed methods are simple, fast and suitable for routine analysis. Acknowledgements: CAPES and CNPq

## Investigation of spectral interferences on the determination of Pb in road dust samples using high-resolution continuum source graphite furnace atomic absorption spectrometry

Susane S. Fick<sup>A</sup>, Flávio V. Nakadi<sup>A</sup>, Patricia Smichowski<sup>B</sup>, Fabián Fujiwara<sup>B</sup>, Maria G. R. Vale<sup>\*A,C</sup>

<sup>A</sup>Instituto de Química, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil; <sup>B</sup>Comisión Nacional de Energía Atómica (CNEA) and Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Buenos Aires, Argentina; <sup>C</sup>Instituto Nacional de Ciência e Tecnologia do CNPq, INCT de Energia e Ambiente, Universidade Federal da Bahia, Salvador, Brazil.

\*mgrvale@ufrgs.br

*The determination of traffic-related elements, especially potentially toxic metals (e.g. lead), in environmental samples such as road dust has become of growing concern in recent years mainly due to the toxicity and persistence of these elements in the environment. There are several spectral interferences in atomic absorption spectrometry (AAS), generally due to the absorption of diatomic molecules. This behavior is mainly observed in direct solid sample (SS) analysis using AAS with graphite furnace (GF) atomization, because there is no previous sample preparation to eliminate the matrix. High-resolution continuum source AAS (HR-CS AAS) provides a detailed view on the surroundings of a specific wavelength, and its resolution enables the visualization of the spectra of diatomic molecules, and methods to correct them if necessary. In this study, spectral interferences on the determination of lead in road dust samples were investigated using HR-CS SS-GF AAS. Due to the high Pb content in the samples, the wavelength 261.418 nm (2.1% relative sensitivity) was selected, with detection of 1 pixel. The samples were collected in Buenos Aires, Argentina, and they were fractionated by particle size, between 37 and 50  $\mu\text{m}$ . Pyrolysis and atomization temperature curves were established with a road dust sample using 10  $\mu\text{g}$  Pd + 6  $\mu\text{g}$  Mg as chemical modifier in solution, and the optimized temperatures were, 900 °C and 2300 °C, respectively. Calibration was with aqueous Pb standard solutions. Different diatomic molecular spectra were observed during sample and reference materials analysis. The AlCl molecule was identified through the software database, and confirmed evaluating the spectrum of an aqueous Al standard solution with HCl. Furthermore, there was a second molecule, which was identified through the literature and tests as SiO, subsequently generated running the GF temperature program with silica. The software offers a least-squares algorithm that corrects background overlap, which could nullify the influence of SiO. The AlCl spectrum was quite different from sample to sample; the lines of the molecular band had a different width and were broader or narrower, leading to a trickier correction. Nevertheless, the use of this correction technique allowed the elimination of the spectral interference, making possible the determination of Pb in the road dust samples. The figures of merit were: characteristic mass of 1.3 ng, and limit of detection and quantification of 0.85 and 2.8  $\text{mg kg}^{-1}$ , respectively, based on a sample mass of 0.8 mg. Relative standard deviation values were below 10% ( $n=5$ ), which is acceptable for direct SS analysis. The accuracy of the method was verified using two certified reference materials, Road Dust (BCR 723) and Soil (NIST SRM 2586); the results were in agreement with the certified values at a 95% confidence level. More investigations on eliminating properly the AlCl molecule interference from the samples will be carried out. Acknowledgements: CAPES and CNPq*

## Determination of thorium in seawater by using SeaFast matrix separation system and Isotope Dilution Inductively Coupled Plasma Mass Spectrometry.

Irena Wysocka <sup>A,B</sup>, Emilia Vassileva <sup>A\*</sup>

<sup>A</sup>International Atomic Energy Agency, Environmental Laboratories, 4 Quai Antoine 1<sup>er</sup>,  
98000 Monaco

<sup>B</sup>Polish Geological Institute National Research Institute, Rakowiecka 4, 00-975 Warsaw, Poland

\* e.vassileva-veleva@iaea.org

**ABSTRACT:** In marine systems, thorium (Th) has proven to be a very useful tracer of a wide range of oceanographic processes and is one of the most important tracers to understand particle dynamics in the ocean. Although a number of Th isotopes exist in seawater, Th consists almost entirely of primordial <sup>232</sup>Th ( $t_{1/2} = 1.4 \times 10^{10}$  years), due to its extremely long half-life relative to the other Th isotopes. Since <sup>232</sup>Th introduced into seawater is rapidly adsorbed on settling particles and removed to sediment, concentrations of <sup>232</sup>Th in seawater are so low (sub-ngL-l levels), that its determination becomes a great challenge. Isotope Dilution Inductively Coupled Plasma Mass Spectrometry (ID ICP-MS), applied as a primary method of measurements has been developed for the determination of ultra-low concentration of dissolved Th in seawater samples. The method is based on matrix separation, analyte preconcentration and determination of <sup>232</sup>Th in a small volume (20 mL) of seawater samples. The application of preliminary sample pre-treatment step, using a commercially available seaFAST-pico system allowed achieving high pre-concentration factor and efficient removal of matrix components. Isotopic ratio measurements were done in off-line mode by a sector field inductively coupled plasma mass spectrometry (ICP-SFMS). The estimated method detection limit was 0.005 ng L-l for <sup>232</sup>Th. The proposed analytical procedure was fully validated and traceability of measurement results demonstrated. Method parameters (selectivity, procedural blank, limit of detection, repeatability, intermediate precision and trueness) were systematically assessed according to ISO-17025 and Eurachem guidelines. The correct assessment of the analytical procedural blank and memory effect were of crucial importance for obtaining reliable results. The analytical procedure was validated in two complementary ways. First, all major sources of uncertainty were identified and propagated together following the ISO/GUM guidelines. Second, the developed method was applied to the seawater reference samples: IAEA-443, SLEW-3, NASS-4 and NASS-6, CASS-5. Although thorium is not certified in any of the seawater reference materials, a good agreement was obtained between obtained in the present study and data published elsewhere. The accurate values and low expanded uncertainties 1.3% -4.5% ( $k = 2$ ) obtained with proposed methodology showed that application of seaFAST-pico combined with ICP-SFMS is a powerful tool, which can be used for <sup>232</sup>Th investigation in seawater.



## **Measurement of Diesel Particulate Matter exhaust emissions generated from real Diesel combustion engine personal vehicles by means of Laser Induced Breakdown Spectroscopy**

Richard Viskup\*, Werner Baumgartner

Johannes Kepler University Linz, Altenberger str. 69, 4040 Linz, Austria

\* Richard.Viskup@jku.at

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*ABSTRACT: Most of the Diesel combustion engine driven vehicles are currently failing to follow the Euro 6 emission standards in real driving environment, due to the strict emission norms. The currently existing European emission standards are the norms for hydrocarbons, carbon monoxide, nitrogen oxides and for particulate matter (PM) from Diesel exhaust emissions, as the total number of all particles. However, there are no other standards for additional compounds or chemical elements contained in the exhaust gas, Diesel Particulate Matter (DPM), or in the soot from the Diesel combustion engine. In this research we apply Laser Induced Breakdown Spectroscopy technique for measurement of DPM, formed from combustion Diesel engine exhaust emissions, mainly concerning the chemical composition of Diesel particulate matter. The aim of this study is to measure the compounds that are present in DPM exhaust emissions generated from real Diesel engine personal vehicles. The presence of these elements in exhaust emission may point to different processes, mainly to insufficient engine combustion process, incomplete catalytic reaction, inefficient Diesel particulate filtering technique, or failure in the Diesel engine. Every information revealed by these studies might be very beneficial for scientists, to better understand the DPM composition, for combustion physics, as well as for engine development engineers in after treatment development, or for the modelling of PM emission generated from Diesel engine vehicles, to meet future emission standards.*

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## Single-particle Investigation of Antarctic Sea Spray Aerosols Using Low-Z particle EPMA, Raman Microspectrometry, and ATR-FTIR Imaging Techniques

Hyo-Jin Eom<sup>A</sup>, Xue Li<sup>A</sup>, HeeJin Hwang<sup>B</sup>, SoonDo Hur<sup>B</sup>, Yeontae Gim<sup>C</sup>, and Chul-Un Ro<sup>\*A</sup>

<sup>A</sup>Department of Chemistry, Inha University, 100 Inha-ro, Nam-gu, Incheon, Republic of Korea; <sup>B</sup>Division of Paleo Environment Sciences, Korea Polar Research Institute, 26 Songdomirae-ro, Yeonsu-gu, Incheon, Republic of Korea; <sup>C</sup>Division of Polar Climate Sciences, Korea Polar Research Institute, 26 Songdomirae-ro, Yeonsu-gu, Incheon, Republic of Korea

\*curo@inha.ac.kr

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**ABSTRACT:** The Antarctic region, which is isolated from anthropogenic sources, is one of the few pristine places to study natural sea spray aerosols (SSAs) with minimum anthropogenic influence [1]. There are conflicting opinions on correlations between levels of chlorophyll-a as an indicator of biological activity in seawater and organic species in SSAs [2-5]. A recent our study [1] showed differences of chemical compositional characteristics between typical summertime and wintertime Antarctic aerosol samples. However, it is not clear whether the different compositional features between two samples are due to their different sampling seasons or biological activities. To better understand about the Antarctic SSAs, additional Antarctic aerosol samples collected during Dec. 2011 and Sep. 2012 when the oceanic chlorophyll-a levels were in the range of 0.07-13.38  $\mu\text{g/L}$  were chosen. Antarctic aerosol samples which are representative for each season with having different chlorophyll-a levels are investigated on a single particle basis using quantitative energy-dispersive electron probe X-ray microanalysis (ED-EPMA), called low-Z particle EPMA, Raman microspectrometry (RMS), and attenuated total reflectance Fourier transform infrared (ATR-FTIR) imaging techniques. Low-Z particle EPMA is applied to get information on morphology and size from SEM images and chemical compositions from X-ray spectra. The two vibrational spectroscopic techniques are used to identify organic and inorganic molecular species through Raman and ATR-FTIR spectra. Detailed characteristics of Antarctic aerosol samples are under examination and will be presented. [1] Eom et al., Atmos. Chem. Phys., 2016, 16, 13823-13836. [2] O'Dowd et al., Nature, 2004, 431, 676-680. [3] Prather et al., Proc. Natl. Acad. Sci. USA., 2013, v110, 19, 7550-7555. [4] Hu et al., Sci. Rep., 2013, 3, 2280. [5] Quinn et al., Nat. Geosci., 2014, 7, 228-232.

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## Determination of benzoic acid and sorbic acid in Vegetables

Sang Soon Yun\*, Sang Jin Lee, Ji Sun So, Gunyoung Lee and MeeKyung Kim

Food Additives and Packaging Division, Ministry of Food and Drug Safety, Cheongju, Korea

\*yss0520@korea.kr

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*ABSTRACT: Benzoic acid and sorbic acid are extensively used and also can be formed naturally in processed food. In this study, rapid determination of naturally formed benzoic acid and sorbic acid in vegetables (lettuce and radish) was performed using HPLC/DAD with confirmation by LC/MS/MS. Benzoic acid and sorbic acid were extracted with ethanol using sonication, then centrifuged and evaporated to dryness. The sample was purified by solid-phase extraction (SPE). A C18 column (4.6 × 150 mm, 5 μm) was used for HPLC/DAD. The method was validated with respect to limit of detection (LOD), limit of quantification (LO), linearity, recovery, and precision. LOD and LOQ were 0.3 mg/kg and 1.0 mg/kg for two analytes, respectively. The calibration curves showed a good linearity with correlation coefficients over 0.999 for two analytes. Recoveries were obtained by spiking standard solution at three different concentrations ranged from 86.0 to 104.2% for benzoic acid and 89.2% to 105.1% for sorbic acid in vegetables. This method can be applied to various vegetable samples to determination of low amounts of naturally occurring benzoic acid and sorbic acid.*

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## Classification of Sand Samples by Using Terahertz Time-Domain Spectroscopy and Chemometrics

Panpan Liu<sup>A</sup>, Xin Zhang<sup>A</sup>, Baolin Pan<sup>B</sup>, Mingjian Wei<sup>B</sup>, Zhuoyong Zhang<sup>\*A</sup>, Peter de B. Harrington<sup>C</sup>

<sup>A</sup>Department of Chemistry, Capital Normal University, Beijing, China; <sup>B</sup>Department of Chemistry, Capital Normal University, Beijing, China; <sup>C</sup>Center for Intelligent Chemical Instrumentation, Clippinger Laboratories, Department of Chemistry and Biochemistry, Ohio University, Athens, Ohio, 45701-2979, USA.

\*gusto2008@vip.sina.com

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**ABSTRACT:** A novel method combining chemometrics with terahertz time-domain spectroscopy (THz-TDS) was proposed for identification of sand samples from different deserts and grain sizes. Terahertz time domain transmittance spectra were collected and then Savitzky-Golay (S-G) and orthogonal signal correction (OSC) were used as pretreatment method, and finally principal component analysis (PCA), partial least squares discriminant analysis (PLS-DA), and support vector machine classification (SVMC) were used to establish classification models. The prediction rates ranged between 90-100%. Scanning electron microscopy (SEM) was used to investigate the differences in morphology. The sand samples were analyzed by using energy dispersive spectroscopy (EDS) and the elemental distributions were obtained. Fourier transform infrared spectra of the sand samples were also collected. THz-TDS combined with multivariate modeling methods provided reliable and useful information to determine the provenance of sands that originated from the Northern China. This work reveals that THz-TDS can be a useful tool for identification of sand from different deserts.

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## Highlighting Flemish and Portuguese painting workshops differences and similarities: two paintings and two masters

Vanessa Antunes<sup>A,B\*</sup>, António Candeias<sup>C,D</sup>, Maria L. Carvalho<sup>B</sup>, Cristina Barrocas Dias<sup>D</sup>, Ana Manhi-ta<sup>D</sup>, Maria J. Francisco<sup>E</sup>, Alexandra Lauw<sup>F</sup>, Marta Manso<sup>B,G</sup>

<sup>A</sup>ARTIS-Instituto História da Arte, Faculdade de Letras, Universidade de Lisboa (ARTIS-FLUL), Alameda da Universidade, 1600-214 Lisboa, Portugal; <sup>B</sup>LIBPhys-UNL, Laboratório de Instrumentação, Engenharia Biomédica e Física da Radiação, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516, Caparica, Portugal; <sup>C</sup>Laboratório José de Figueiredo, Direcção-Geral do Património Cultural (LJF-DGPC), Rua das Janelas Verdes 37, 1249-018 Lisboa, Portugal; <sup>D</sup>Laboratório HERCULES, Escola de Ciências e Tecnologia, Universidade de Évora, Largo Marquês de Marialva 8, 7000-676 Évora, Portugal; <sup>E</sup>Museu de Setúbal - Balneário Dr. Paula Borba 2900 -120 / Setúbal / Portugal; <sup>F</sup>Centro de Estudos Florestais, Instituto Superior de Agronomia, Tapada da Ajuda, 1349-017 Lisboa, Portugal; <sup>G</sup>Faculdade de Belas-Artes, Universidade de Lisboa, Largo da Academia Nacional de Belas-Artes, 1249-058 Lisboa, Portugal.

\* vanessahantunes@gmail.com

**ABSTRACT:** This work compares the materials and the techniques employed by two artists in two paintings with different origin, Flemish and Portuguese, but concerning the same theme. The common theme is the “Apparition of the angel to Santa Clara, Santa Inês and Santa Coleta” leads to believe that one of the paintings might have originated the other. The Flemish painting is assigned to Quentin Metsys (1466-1530), made circa 1491-1507, being probably a gift from the emperor Maximilian to his cousin queen D. Leonor who offered the painting to Convento de Jesus, in Setúbal, Portugal. The nuns from this convent would have commissioned a painting with the same theme to Jorge Afonso (c. 1470-1540), the most important painter of Lisbon workshop (1517-19/1530) being this altarpiece his last and most significant work [1, 2] The aim of this study is to compare the materials and the techniques of Flemish and Portuguese workshops to determine their differences and similarities. Was the Portuguese painter Jorge Afonso influenced by the Flemish techniques, or has he followed the Portuguese workshops concerning techniques and materials? To perform this study, the materials were analysed by portable X-ray fluorescence spectroscopy,  $\mu$ -X-ray diffraction, Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy,  $\mu$ -Confocal Raman and High Performance Liquid Chromatography coupled to Diode-Array and Mass Spectrometry detectors. Pigments found in both paintings were similar but ground layers differed in their constitution, as the overlapping of the pigment layers. The differences and similarities between both paintings showed that he followed the Flemish tradition by using certain materials such as the Baltic oak of the support and similar pigments but a differentiation in the use of ground layer materials and overlapping of pigment layers technique. This study brings a new insight to the tendencies of Flemish and Portuguese paintings, highlighting Flemish influences in the Portuguese painting concerning materials and painting techniques. [1] F.A. Baptista Pereira, *A pintura num período de transição*, in: D. Markl (Ed.) *História da arte em Portugal-O Renascimento*, Alfa, Lisboa, 1986, pp. 83-155. [2] F.A.B. Pereira, M. Batoréo, A.N. Alves, A. Jesus, M.J. Francisco, *Retábulo do Convento de Jesus de Setúbal*, Câmara Municipal de Setúbal, 2013.

## Characterization of polymeric biomaterial for high-resolution X-ray Imaging

A.Antunes<sup>\*A,B</sup>, I. L. Ferreira<sup>A</sup>, A.F.G. Monte<sup>A</sup>, Maria Raposo<sup>B</sup>

<sup>A</sup>Instituto de Física, Universidade Federal de Uberlândia, Uberlândia, Brazil; <sup>B</sup>Departamento de Física - Faculdade de Ciências e Tecnologia, Universidade, Nova de Lisboa, Campus da Caparica, Portugal.

\*andrea.antunes@ufu.br

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**ABSTRACT:** *In this investigation, diffraction enhanced imaging (DEI), a synchrotron radiation technique, was used to characterize polymeric biomaterials. We have produced biomaterials using chitosan and gelatin as major components varying their concentration. 3D biomaterials samples were confectioned and structural alterations were monitored to distinct preparation conditions. The images of the samples were taken at 20 keV using the silicon (3,3,3) reflection in equally to the monochromator and analyzer system. High resolution imaging was carried out at the X15A beamline at the National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY. Several images were acquired at various analyzer angle positions. Our results have indicated that DEI was a technique with spatial resolution adequate showing details about structural alterations.*

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## Metabolomic approach investigating differences in two generation of genetically modified and non-modified soybean seeds

Bruna Campos<sup>\*A</sup>, Rodrigo Galazzi<sup>A</sup>, Fábio Santos<sup>B</sup>, Marcos Eberlin<sup>B</sup>, Marco Arruda<sup>A</sup>

<sup>A</sup> Spectrometry, Sample Preparation and Mechanization Group – GEPAM, Institute of Chemistry, University of Campinas – UNICAMP, P.O. Box 6154, Campinas, SP, 13083-970, Brazil; <sup>B</sup> ThoMSon Mass Spectrometry Laboratory, Institute of Chemistry, University of Campinas – UNICAMP, Campinas, SP, 13083-970, Brazil.

\*brunah.campos@hotmail.com

**ABSTRACT:** Genetically modified (GM) organisms greatly improve the growing and harvest when considering soybeans. However, recent studies involving GM soybeans have been demonstrating that the insertion of an exogenous gene (currently that one conferring resistance to glyphosate) into the DNA provokes some changes in biological and chemical characteristics [Arruda et al., 2013; Barbosa et al., 2013]. As it is well known that farmers keep some seeds from the last harvest to be cropped to the next one. Due to this fact in addition to some changes in such organisms pointed out in the literature, as commented, our hypothesis is that such changes can be propagated to different generations. In this context, we carried out a comparative metabolic profile between non-modified or non-transgenic - NT (MSOY 7211RR) and GM (MSOY 8200) seeds resistant to glyphosate from different generations of soybean. For this, plants (NT and GM) were grown in a greenhouse from January to May of 2014 and 2015 to obtain the second (2G) and third generations (3G) of seeds, respectively. The seeds were frozen and macerated in liquid nitrogen. From 0.1 g of seeds the metabolites were extracted into 1 mL of MeOH/water (70:30%, v/v). Then, the mixture was ultra-sonicated for 1 min (10 s on-off) in a cup-horn system employing 50% amplitude and centrifuged for 5 min at 13000 g. The metabolites were analyzed by UHPLC-MS using an Agilent 1290 Infinity Binary LC system coupled to an Agilent 6550 Accurate-Mass Q-TOF system and with Agilent Jet Stream electrospray ionization. For the chromatographic separations, 3 µL of the extract were injected in the column XB-C18 Kinetex (150 x 2.1 mm, 1.7 µm particles). Mobile phases were constituted by 0.1% formic acid in water (A) and 0.1% formic acid in acetonitrile (B) at total flow rate of 400 µL min<sup>-1</sup>. Chromatographic elution was 25 min at a linear gradient of 5-95% of mobile phase B. Total ion spectra were collected over a 100–1500 of m/z mass range, in both negative and positive modes. The Q-TOF MS optimized parameters were: acquisition rate (1.0 spectra/s), Drying gas temperature (290 °C), Drying gas flow rate (14.0 L/min), Sheath gas temperature (250 °C), Sheath gas flow rate (12.0 L/min), Nebulizer gas (45 psi), Skimmer voltage (65 V), Octopole RF (750 V), Fragmentor (150 V), Capillary voltage (3.0 kV), and Nozzle Voltage (350 V). Collision induced dissociation (CID, 30 eV) MS/MS analysis of individual compound was further conducted to confirm these compounds. Chromatograms were processed by XCMS software and multivariate analyses were performing using the MetaboAnalyst 3.0 (version software). Applying the principal component analysis (PCA)-derived scores plot was possible to discriminate four well defined clusters corresponding to each treatment: transgenic or non-transgenic cultivars and both from second and third generations. Close clustering of the three biological replicates per species that indicates high reproducibility were also observed. Major differences between GM and NT groups were displayed by PC1 and differences between second and third generations were displayed by PC2 based on the metabolites groups. PCA-derived loading plots showed major metabolites which were responsible for the differentiation of GM and NT clusters as well as the generations belonged to different chemical groups, mainly, carbohydrates, lipids, flavonoids, fatty acids and amino acids. Two main blocks of metabolites were clearly identified through heatmap: the first block a group of metabolites was detected, which present high abundance to those seeds of GM group. Such abundance decreased for NT group, independent of the generation evaluated. On the other hand, the metabolites of the second block showed an increased abundance in NT group. The next step is to do the identification of ions that are discriminating the GM or NT from 2nd and 3rd generations samples. Herein, we can conclude that major differences can be found at molecular levels not only between GM and NT soybean seeds but also between their generations.

## Fourier Transform Infrared Spectroscopy in the leather quality control (LIFE14 ENV/IT/000443 LIFETAN)

Marco Carlo Mascherpa<sup>A\*</sup>, Massimo Onor<sup>A</sup>, Beatrice Campanella<sup>A,B</sup>, Alessandro D'Ulivo<sup>A</sup>, Emanuela Pitzalis<sup>A</sup>, Elena Salernitano<sup>C</sup>, Alessandra Strafella<sup>C</sup>, Alice Dall'Ara<sup>C</sup> and Emilia Bramanti<sup>A</sup>

<sup>A</sup> Institute of Chemistry of Organo Metallic Compounds (ICCOM)- U.O.S. Pisa, Italian National Research Council (CNR), Via G. Moruzzi 1, 56124 Pisa; <sup>B</sup> University of Pisa, Department of Chemistry and Industrial Chemistry, via Moruzzi 13, 56124 Pisa, Italy; <sup>C</sup> Laboratory of Materials Technologies Faenza (TEMAF), Italian National agency for new technologies, Energy and sustainable economic development (ENEA), Via Ravegnana 186, 48018 Faenza (Italy).

\*mascherpa@pi.iccom.cnr.it

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**ABSTRACT:** LIFETAN project is aimed at demonstrating the use of innovative natural products and technologies in the leather tanning process. The current commercial chemicals employed in the tanning process are very toxic and have a big impact on the environment. For this reason EU supports Life+ Program in order to replace products/processes with eco-sustainable and convenient ones to propose "green" industrial cycles. LIFETAN implements the results obtained in five previous Life+ projects and demonstrates the use of new natural products at laboratory, semi-industrial and industrial phase. The goals are to propose products with higher biodegradability and performance to produce high quality leather products better or comparable with those obtained employing traditional ones. Spectroscopic techniques are fundamental in the monitoring actions to characterize the leather samples. In particular FTIR is a valuable useful technique to investigate at molecular level the interaction of new products with the leather proteins. The FTIR analysis of amide I band gives information both in terms of the absorbance ratios at two different wavelengths (e.g. the 1654/1690 cm<sup>-1</sup> absorbance ratio to evaluate the collagen cross linking) and the analysis of the single components found by peak fitting (conformational analysis). The results obtained on several LIFETAN samples processed with the new tanning formulations are described. These experimental results are also confirmed by Scanning Electron Microscopy (SEM) observations, Energy Dispersive X-Ray Spectroscopy (EDS) microanalysis and Thermogravimetric Analysis (TGA). (The Life 14 ENV/IT/443 LIFETAN project is co-financed by EU, within the LIFE program)

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## Megapixel multi-elemental imaging by Laser-Induced Breakdown Spectroscopy, a technology with considerable potential for paleoclimate studies

J. O. Cáceres<sup>A\*</sup>, V. Motto-Ros<sup>B</sup>, S. Moncayo<sup>A,B</sup>, F. Trichard<sup>B</sup>, F. Pelascini<sup>C</sup>, G. Panczer<sup>B</sup>, A. Marín-Roldán<sup>A</sup>, S. Manzoor<sup>A</sup>, J. Cruz<sup>D</sup>, I. Coronado<sup>E</sup>, J. Martín-Chivelet<sup>D,E</sup>

<sup>A</sup>Química Laser, Dpto. De Química Analítica, Fac. De CC Químicas, Universidad Complutense, 28040 Madrid, Spain ; <sup>B</sup>Institut Lumière Matière, UMR5306 Université Lyon 1-CNRS, Université de Lyon 69622 Villeurbanne cedex, France; <sup>C</sup>CRITT Matériaux Alsace, 19, rue de St Julien, 67305 Schiltigheim, France ; <sup>D</sup>Dpt. Estratigrafía, Fac. Ciencias Geológicas, Universidad Complutense de Madrid, 28040 Madrid, Spain; <sup>E</sup>Instituto de Geociencias (CSIC, UCM), C/ José Antonio Nováis 12, 28040 Madrid, Spain.

[\\*jcaceres@ucm.es](mailto:jcaceres@ucm.es)

**ABSTRACT:** Paleoclimate studies play a crucial role in the understanding of the past and future climate and its environmental impacts<sup>1</sup>. The analysis of variations in the concentration of trace elements such as Sr, Na, Mg during the growth of carbonate proxies has a high potential as a tool for reconstructing past changes in hydrology, rainfall, and temperature. For the spatial resolution in these analyses at the required performance (ppm,  $\mu\text{m}$ ), current elemental technologies such as synchrotron radiation microanalysis (SXRF), nano-secondary ion mass spectrometry (nano-SIMS) or laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) are restricted to the use of complex and not easily accessible techniques<sup>2-4</sup>. Herein, we present the megapixel LIBS in the study of variations in trace elements at micro- and macroscales in coral (*Scleractinian Coral - Dendrophyllia ramea*) and speleothem sample. A Q-switched Nd:YAG-laser is successfully applied to perform fast multielemental scanning of geological samples with high performance in terms of sensitivity. The signals were processed to generate multielemental images of the spatial distribution of elements in the sample surface of a big stalactite and a coral sample. The compositional changes in Mg and Sr followed the patterns of the speleothem stratigraphy, demonstrating that compositional variations are determined by temporal changes in hydrogeochemical conditions during stalagmite growth. The main biological structures of the coenosteum and the septa of each corallite are perfectly recognizable and the possibility to finely resolve the complex growth mode of coral and its inner structure of the dendroid colony by the elemental images was demonstrated. The LIBS images helped in the choice of the sampling strategy which is critical in obtaining representative climatic records, avoiding the center of calcifications (COCs) that hinder the climatic information. The walls of the central branch show compositional variations along the growth axis (Sr/Ca, Mg/Ca, Na/Ca) that probably record several decades of climatic and environmental information. The technique opens vast opportunities for generating new additional high-resolution paleoclimate records from samples of a wide range of ages and provenances. [1] G.C. Rau, M. O. Cuthbert, M.S. Andersen, A. Baker, H. Rutledge, M. Markowska, H. Roshan, C.E. Marjo, P.W. Graham, R.I. Acworth, *Quat. Sci. Rev.* 127 (2015) 19-36. [2] W. Chao, B.D. Harteneck, J.A. Liddle, E.H. Anderson, D.T. Attwood, *Nature* 435 (2005) 1210-1213. [3] M.L. Kraft, H.A. Klitzing, *Biochim. Biophys. Acta.* 1841, (2014) 1108-1119. [4] M. Zoriy, M. Dehnhardt, A. Matusch, J.S. Becker, *Spectrochim. Acta B.* 63 (2008) 375-382.

## Evaluation of the surface intermediates during the methane catalytic combustion over non-noble catalysts by *in situ* NIR and 2D-COS

Damian K. Chlebda <sup>\*A</sup>, Przemysław J. Jodłowski <sup>B</sup>, Roman J. Jędrzejczyk <sup>C</sup>, Anna Dziejicka <sup>B</sup>, Dominika Pawcenis <sup>A</sup>, Joanna Łojewska <sup>A</sup>

<sup>A</sup> Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Kraków, Poland; <sup>B</sup> Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 30-155 Kraków, Poland; <sup>C</sup> The Malopolska Centre of Biotechnology, Jagiellonian University, ul. Gronostajowa 7A, Kraków, Poland

\*damian.chlebda@uj.edu.pl

**ABSTRACT:** The catalytic combustion has become the most commonly used method for the gas exhaust abatement within many technological applications [1]. Nowadays, the new trend to the rational optimisation of the working catalyst preparation demands the knowledge of the evolution of the reaction intermediates at the catalyst surface. The catalytic reaction involves many sites or areas on the catalyst surface that are able to interact with one another leading to self-organization in space and time. Thus, the characterisation of the catalyst behaviour during the reaction is a crucial step in the catalyst optimisation. The most adequate way to monitor the changes in the catalysts structure during the reaction is the application on the *in situ* and *operando* spectroscopic methods [2]. The last decade brought a relevant improvement of the *in situ* measurements i.e. due to the mimic of the reaction condition in the real systems, and thus expanded the applicability of the vibration spectroscopy for monitoring the progress of the reaction. However, when considering the multicomposite systems, the *in situ* quantitative determination of the active sites may become difficult. One of the method that may be used to simplify the analysis of complex spectra is two-dimensional correlation spectroscopy (2D-COS). The 2D-COS has attracted much popularity among the researchers within last several decades, especially for the analysis of complex NMR spectres. In this study, the *in situ* homospectral two-dimensional correlation spectroscopy was used to evaluate the intermediates appearing at the catalysts surface during the catalytic combustion of methane over various metal oxide structured catalysts. The series of cobalt, cerium and palladium nanocomposite structured catalysts were prepared on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> via impregnation method. 2D-COS is found to be a powerful tool for the improvements the *in situ* characterisation of surface species presented on a working catalyst. The employment of mathematical transformation of spectra allows to establish the sequence of event and in detail describe the progress of the reaction over structured catalysts.

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## Automatic classification of metal alloys from their LIBS spectra and its robustness against spectrometer decalibration

Adolfo Cobo<sup>\*A</sup>, Artzai Picón<sup>B</sup>, Marina Martínez<sup>A</sup>, Cristina López-Sarachaga<sup>B</sup>, Zuriñe Amondarain<sup>B</sup>, José Miguel López-Higuera<sup>A</sup>

<sup>A</sup>Photonics Engineering Group, University of Cantabria, 39005 Santander, Spain; <sup>B</sup>Tecnalia, Parque Tecnológico de Bizkaia, 48160 Derio- Bizkaia, Spain

\*adolfo.cobo@unican.es

**ABSTRACT:** Among the most successful applications of LIBS in the industry is the analysis of metal alloys and steel, mainly due to the rich information in the emitted spectra from minor and major constituents of the alloys, and the possibility of online, remote, and automated analysis. This opens the possibility of applications such as online quality monitoring of steel production [1] or automated metal scrap sorting [2]. For these tasks, the raw spectra should be processed and transformed into meaningful information, such as composition, quality deviations or detection of valuable, toxic or specific elements, and several chemometric or artificial-intelligent based techniques have been proposed [3]. All these approaches should cope with the possibility of long-term wavelength decalibration of the spectrometer, especially for low-cost CCD spectrometers and in the tough manufacturing environment.

In this work, we report on the automatic classification of steel alloys samples based on their LIBS spectra generated with a Nd:YAG laser @ 1064nm and captured in the 240-518nm spectral range. The samples have been manufactured in a levitation melting induction furnace and contains different known percentage of single elements in iron: C, P, Mo, S, Mn, Cr, Cu, Sn, Si, Ni, and Al. The thousands of LIBS spectra collected from each sample have been used to train a deep autoencoder neural network [4] to perform the classification, and performance numbers have been obtained. As only the raw spectra with no peak identification or modelling have been passed onto the classifier, the classification rate decreases significantly if data from experiments in different days with small wavelength decalibration is used to validate the trained network. To ensure the long-term operation in a real application, several approaches have been tested, among others: periodic auto-recalibration based on the iron emission lines, data augmentation with purposely decalibrated spectra for the network training or Bayesian estimation of the deviations on the calibration function on a fully Bayesian approach. Results show the robustness of these approaches.

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## Quantification of Carbon in Steel using Handheld LIBS

Brendan Connors and David R. Day\*

SciAps, 2 Constitution Way, Woburn, MA, 01801, USA

\*dday@sciaps.com

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*ABSTRACT: X-Ray fluorescence handheld analyzers have been available for nearly two decades for metal alloy analysis. However, they have lacked the ability to measure the low atomic weight elements. Recently handheld LIBS analyzers, which are very sensitive to light elements, have helped with many of those prior limitations including, for example, the measurement of lithium in aluminum. There is still a very large need to measure carbon content in low alloy steels with handheld instrumentation. Until now, the quantitative measurement of carbon in steel has been left to large arc-spark OES type instrumentation. In this work we describe the development of a handheld analyzer method for quantitative carbon analysis down to 1000ppm levels using the carbon 193 nm emission line. The method also takes advantage of time gating on the order of 1 microsecond and argon purging from a self-contained argon cartridge within the handheld instrument. Calibration and validation results from certified reference standards and scrap yard samples will be presented.*

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## Nanoparticles-Enhanced Laser-Ablation ICP-MS Of Metals

F. Mastrorocco<sup>1</sup>, L.C. Giannossa<sup>2</sup>, C. Koral<sup>1</sup>, A. De Giacomo<sup>1</sup>, A. Mangone<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Bari Aldo Moro, Via Orabona 4, Bari (Italy); <sup>2</sup>Department of Economics, Management and Business Law University of Bari Aldo Moro, Largo Abbazia Santa Scolastica 53, 70124 Bari (Italy)

annarosa.mangone@uniba.it,

**ABSTRACT:** This research shows a preliminary study of nanoparticles-enhanced LA-ICP-MS. The aim is to obtain an analytical procedure able to improve the analytical performance of the technique in terms of sensitivity and LOD, without any changes of the experimental set up. Indeed, laser parameters or kind and flow of gas carrier can be changed to improve the amount of the ablated sample; otherwise, the sample can be altered, preserving its chemical properties, in order to increase its response to laser. The undoubted strength of this approach, adopted by us, is represented by its simplicity, affordability and fast performance.

Some drops of Au nanoparticles (AuNPs) colloidal dispersion were deposited on the sample's surface, the solvent was evaporated and the sample analyzed by LA-ICP-MS. Different metallic elements (Cu, Zn, Sn, Pb...) in various substrates (metals, copper-based alloys, and glass) were analyzed.

A remarkable increase in the measured signal intensity for all the analyzed sample was observed due to the presence of AuNPs. As a consequence of the signal enhancement, the sensitivity was always improved (about 1 order of magnitude with respect to the conventional LA-ICP-MS) -though to different extents according to the experimental conditions and the examined sample- and the LOD decreased significantly. In analogy of what has already proved with Laser Induced Breakdown Spectroscopy [1,2], when a critical number of NPs are deposited on the target surface, the laser pulse electromagnetic field induces the collective oscillation of the conduction electrons of the NPs that in turn results in a strong enhancement of the field. The latter allows to switch the seed electron production in the ablation process from multiphoton ionization to electron field emission. In this frame a more efficient and homogeneous ablation can be obtained.

The remarkable increase in the measured signal intensity will allow to determine traces and ultratraces in extremely small sample of various complex matrices (environmental, forensic, clinical, food analyses, cultural heritage) with no sample pretreatment.

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## Fluid-dynamic Design of Laser Ablation Chambers for Laser Ablation-Laser Induced Breakdown Spectroscopy (LA-LIBS).

Daniel Diaz<sup>\*A</sup>, David Soto<sup>A</sup>, David Hahn<sup>B</sup>, Alejandro Molina<sup>A</sup>

<sup>A</sup> Facultad de Minas, Universidad Nacional de Colombia- Sede Medellin, Cra. 80 #63-223 Medellín, Colombia;

<sup>B</sup> Department of Mechanical and Aerospace Engineering, University of Florida, Gainesville, Florida 32611, USA.

\*dhdiazo@unal.edu.co

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*ABSTRACT: Design parameters of laser ablation chambers for chemical analysis of metallic alloys using LA-LIBS were established and optimized through computational fluid dynamics (CFD) simulations. The main variables influencing the chamber performance were its shape and volume, the carrier gas type and the location of the sample and the ablated particles relative to the extraction site. The gas flow in drum- and tube-shaped chambers was evaluated for N<sub>2</sub>, Ar and He carrier gases. Particle-free CFD simulations showed the geometry and carrier gas that guaranteed the shortest residence time. A second set of simulations included particles. The ablated particles sizes were described by the Rosin-Rammeler distribution and were introduced as a discrete phase ejected from the sample surface represented by a cone-type injection. Lower residence time and higher particle extraction were obtained in the tube-shaped chamber with He as carrier gas. The fact that a simple CFD analysis significantly improved the chamber fluid dynamics suggests that the performance of LA-LIBS can also be improved by proper chamber design that minimizes sample dilution as most LA-LIBS setups evidence significant dilution because they use conventional drum-type chambers to transport the ablated particles. The methodology and results of this research are also applicable to any technique that uses LA as sampling approach such as inductively-coupled plasma mass spectrometry (LA-ICP-MS).*

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## Quantification of halogens in concrete using molecular emission

Thomas Dietz<sup>A</sup>, Cassian Gottlieb<sup>B</sup>, Nina Sankat<sup>B</sup>, Gerd Wilsch<sup>B</sup>,  
Christian Bohling<sup>C</sup>, Peter Kohns<sup>A</sup>, Georg Ankerhold<sup>\*A</sup>

<sup>A</sup>University of Applied Sciences Koblenz, RheinAhrCampus,  
Joseph-Rovan-Allee 2, 53424 Remagen, Germany; <sup>B</sup>Bundesanstalt für Materialforschung und -prüfung (BAM),  
Unter den Eichen 87, 12205 Berlin, Germany; <sup>C</sup>SECOPTA analytics GmbH, Ostendstrasse 25, 12459 Berlin,  
Germany.

\*[ankerhold@hs-koblenz.de](mailto:ankerhold@hs-koblenz.de)

**ABSTRACT:** We present the industrial collaboration project "HaloLIBS" for the development of a highly-sensitive LIBS method to detect halogens in reinforced concrete. The diffusion of chloride from de-icing salt into the concrete can provoke a corrosion of the steel-reinforcement (pitting corrosion). If the chloride contamination exceeds a certain level, this can result in a reduced stability and hence to a drastically shortened lifetime of infrastructure buildings like bridges or parking decks. Spatially resolved techniques to quantitatively determine the local chloride concentration are required to estimate the demand of restoration. The conventional wet-chemical analysis is precise but cost- and time-consuming. Moreover, it cannot reveal chloride diffusion profiles alongside the concrete drilling core. The detection of atomic chlorine is a challenging task that needs sophisticated LIBS setups and measurements under helium atmosphere [1,2]. With time-resolved LIBS as an alternative method, we monitor the strong molecular emission of calcium chloride radicals (CaCl) formed during the plasma-cooling phase [3]. This can be performed without any sample preparation in ambient air. The quantification of the local distribution of halogens is deduced by multivariate statistics of the molecular spectral information. The Federal Institute for Materials Research and Testing (BAM) is responsible for the development of multiphase reference standards for quantification of halogens. The University of Applied Sciences Koblenz is developing the experimental LIBS setup for time- and space-resolved measurements and is simulating the radical formation process in the plasma-cooling phase to develop an appropriate quantitative analysis algorithm incorporating environmental parameters. SECOPTA analytics GmbH as the industrial partner is responsible for the development of a time-resolving polychromator to detect atomic and molecular emission. For the automated data evaluation, different chemometric methods for microcontrollers will be developed. **Acknowledgments:** This project is supported by the German Federal Ministry for Economic Affairs and Energy (BMWi), ZIM project grant No KF26821030F4.

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## Qualifying a Commercial LIBS Instrument for Method Validation in Metallurgical Industries

François R. Doucet\*<sup>A</sup>, Lütfü-Çelebi Özcan<sup>A</sup>

<sup>A</sup>ELEMISSION Inc., 108-4030, Côte-Vertu, Montréal, QC, CANADA, H4R 1V4;

\*fdoucet@elemission.ca

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**ABSTRACT:** The metal industry has been using Spark-AES (Atomic Emission Spectroscopy) for more than 70 years for controlling the chemical composition of their alloy production. The Spark-AES technology is now considered mature; nevertheless it still requires the mechanical preparation of the surface prior analysis. Automation have improved the repeatability of the technology as well as lowering human error, however, direct analysis of process stream is very challenging, and probably impossible. On the other hand, Laser-Induced Breakdown Spectroscopy is an emerging technology for controlling the chemical composition of the metallurgical process stream. Several groups have developed solutions that enable the direct analysis of metal on the process using LIBS technology with encouraging performances. In addition, several attempts to validate an analytical procedure for analysis of steel and aluminum have been made by the LIBS community without success. The uses of experimental instruments without any care of the instrument thermal drift, as well as the use of insufficient resolution are probably the main reasons why these attempts failed. In this communication, a novel commercial LIBS instrument that deliver the required performance for a method and procedure validation will be presented. This novel LIBS analyzer has the capability to analyse the sample without sample preparation in few seconds. In addition, this instrument has demonstrated repeatability and reproducibility better than 1% and 3% respectively on the alloying elements in steel and aluminum. This new LIBS instrument has demonstrated multiple correlation coefficients ( $R^2$ ) better than 0.9999 for the most common alloying elements in steel and aluminum. Finally, this new LIBS analyzer has demonstrated to deliver accuracy better than 4% on several external validations made on certified reference material.

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## Sonochemically assisted synthesis of zeolite catalysts for methane combustion

Anna Dziedzicka<sup>\*A</sup>, Łukasz Kuterasiński<sup>A</sup>, Roman J. Jędrzejczyk<sup>B</sup>, Damian Chlebda<sup>C</sup>,  
Przemysław Jodłowski<sup>A</sup>

<sup>A</sup>Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 30-155 Kraków, Poland; <sup>B</sup>The Malopolska Centre of Biotechnology, Jagiellonian University, ul. Gronostajowa 7A, Kraków, Poland; <sup>C</sup>Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Kraków, Poland

\*dziedzicka@indy.chemia.pk.edu.pl

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**ABSTRACT:** Nanostructured transition metal oxides due to their specific magnetic, optical and catalytic properties have been under vigorous investigation over the years [1-2]. From a wide range of possible applications of nanoparticles, the catalysis seems to be the most beneficiary and exploited field. The nanoparticle synthesis can be performed by using such methods as: chemical reduction, sputtering, chemical dealloying, microwave assisted synthesis or deposition methods (CVD, PVD). Here, we present the in situ sonochemically assisted synthesis method of catalysts preparation. The versatility of sonochemical method of nanoparticle preparation was confirmed in a wide range of applications. The recent literature studies have proven that sonochemistry can be successfully applied for a catalysts synthesis for various applications [3]. The aim of this study was to investigate the sonochemical method for the preparation of the zeolite-based catalysts containing copper, iron and cobalt that would be active in methane catalytic combustion. The obtained catalysts were characterised by XRD, BET nitrogen adsorption, XRF, SEM/EDX, TEM and  $\mu$ Raman. The nanoparticle formation directly on the zeolite support was proposed and investigated. The proposed catalyst synthesis had demonstrated its great properties towards the preparation of nanocrystalline catalysts. The TEM analyses results revealed that the catalysts crystallite sizes were in a range of 60-130 nm. The activity of prepared catalysts was determined in methane catalytic combustion. The supported cobalt catalysts have revealed great activity towards the methane catalytic combustion. 1. N. Zheng and G. D. Stucky, *J. Am. Chem. Soc.*, 2006, 128, 14278–14280. 2. M. B. Gawande, A. Goswami, F. X. Felpin, T. Asefa, X. Huang, R. Silva, X. Zou, R. Zboril and R. S. Varma, *Chem. Rev.*, 2016, 116, 3722–3811 3. S. Allahyari, M. Haghighi, A. Ebadi and S. Hosseinzadeh (2014) *Ultrason Sonochem* 2014, 21, 663–673 The Project was financed by the National Science Centre Poland based on the decision No 2015/17/D/ST8/01252 and partly within National Centre for Research and Development No LIDER/204/L-6/14/NCBR/2015.

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## Effect of steel temperature and corrosion on laser-induced plasma of the salt deposit

S. Eto\*, T. Fujii

Central Research Institute of Electric Power Industry, 2-6-1 Nagasaka, Yokosuka, Kanagawa, 240-0196 Japan

\*eto@criepi.denken.or.jp

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**ABSTRACT:** The effect of laser-induced breakdown spectroscopy (LIBS) measurement of salt, deposited on a stainless-steel plate, on the environmental condition was evaluated. The emission intensities of elements in salt did not strongly depend on the surface temperature of a steel plate when the plate was heated up to 200 degree Celsius. On the other hand, the emission intensity of all elements in salt and air (oxygen) decreased when the steel was eroded uniformly.

Concrete cask is one of the dry storage systems of spent fuel. The stainless-steel canister inside the concrete body is cooled down by the natural ventilation system. It is possible to occur the stress corrosion cracking at the surface of the stainless-steel when sea salt particles enter the ventilation system and the chloride ion concentration on the stainless-steel becomes higher than the threshold value for occurring the cracking. Since the measurement of chloride ion concentration is important to evaluate the occurrence of the stress corrosion cracking, we proposed the laser-induced breakdown spectroscopy (LIBS) system for the measurement of chlorine in salt deposited on the stainless steel [1]. Recently, a robot system have been developing to inspect the surface of the canister by combining an eddy current method, temperature monitoring and LIBS [2]. It is considered that the canister is heated up to 200 degrees Celsius and eroded due to the salt deposition during the long-term storage. When LIBS is applied to the measurement of salt deposited on the surface of the canister, the environmental condition such as the high temperature and the erosion of the canister should be considered.

The heating system was constructed to heat a steel plate on which sea salt particles were deposited. The effect of high temperature of the stainless-steel plate on the emission intensity was evaluated by using the heating system and LIBS setup. In addition, steel plates were set in an environmental test chamber with a temperature of 80 degree Celsius and a relative humidity of 30 % to erode the plate.

When the surface temperature of the stainless-steel was changed from 22 to 200 degrees Celsius, the emission intensities of elements in the sea salt did not strongly depend on the surface temperature of the plates. On the other hand, the emission intensities depended on the corrosion condition of the steel plates, and decreased drastically at the position at which the steel was eroded deeply.

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## Internal Standardization Enabling Calcium Determination In Biochar Soil Conditioners By Laser-Induced Breakdown Spectroscopy

Carla Pereira de Morais<sup>A</sup>, Ariane Isis Barros<sup>A</sup>, Dário Santos Júnior<sup>B</sup>, Clóvis Augusto Ribeiro<sup>A</sup>,  
Giorgio Saverio Senesi<sup>C</sup>, José Anchieta Gomes Neto<sup>A</sup>, Edilene Cristina Ferreira<sup>A\*</sup>

<sup>A</sup>Departamento Química Analítica, Universidade Estadual Paulista, Araraquara, São Paulo, Brazil; <sup>B</sup>Departamento de Química, Universidade Federal de São Paulo, Diadema, São Paulo, Brazil; <sup>C</sup>CNR, Istituto di Nanotecnologia (NANOTEC) - PLasMI Lab, Bari, Italy.

\*edilene@iq.unesp.br

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*ABSTRACT: Biochar has gained agricultural importance as a soil conditioner because it is produced from recycled materials and shows important properties such as water retention, plants nutrients supplier, microorganisms growth supplier and atmospheric CO<sub>2</sub> sequestrant. Further, due to its active sites, biochar can adsorb nutrients, boosting its property as soil conditioner. In the frame of quality control, the rapid assessment of nutrients in biochar soil conditioners is essential for agricultural purposes. Thus, the objective of this work was to develop a simple and fast analytical method based on Laser-Induced Breakdown Spectroscopy (LIBS) to determine Ca in biochar soil conditioners. To this purpose, biochar samples added with Ca were prepared from peanut shells, residues of eucalyptus and banana fibers. The calibration standards were prepared by matrix matching using biochar from residues of eucalyptus. The strong matrix effects demanded a strategy to enable quantitative determination, which was reached by using internal standardization. The plots of the ratio between Ca (analyte) and Na (internal standard) as a function of Ca concentration in standards, showed a linear correlation coefficient of 0.98 and a linear work range of 1.63-10.4 % Ca. The limits of detection and quantification of the method developed were respectively 0.82% e 2.26%. The Ca contents determined in prepared soil conditioners were in agreement with those measured by high-resolution continuum-source atomic absorption spectrometry (paired t-test at 95% confidence level). The method developed stressed the importance of internal standardization and matrix matching for quantitative analysis by LIBS and was successfully applied for Ca determination in a complex matrix like biochar soil conditioners produced from different biomasses.*

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## Material properties and their impact on laser-induced plasmas for concrete analysis

Cassian Gottlieb\*, Tobias Günther, Gerd Wilsch

Bundesanstalt für Materialforschung und –prüfung (BAM), Unter den Eichen 87, 12205 Berlin, Germany

\*cassian.gottlieb@bam.de

**ABSTRACT:** Concrete as a porous and multiphase material is made of coarse aggregates (grain size between 0.125 mm and 32 mm), flour grains (aggregates with a grain size below 0.125 mm), cement (grain size < 50 µm) and water. The use of different grain sizes by making concrete is important to ensure the needed density and compressive strength. As a result of making concrete the porous cement matrix contains a mixture of flour grains and cement particles (micro-heterogeneity) and because of the capillary pore space, ion transport can take place. If harmful species like alkali or chlorides penetrate through the pore space, they may trigger different damage processes. The remaining lifetime of concrete structures is estimated due to the quantification of element concentrations regarding to the cement matrix only. In the evaluation of concrete using LIBS a two-dimensional evaluation is necessary to consider the heterogeneity [1-2]. A correlation between physical properties like sample grain sizes and their effect on the quantification will be presented [3-5]. Strategies to consider the micro-heterogeneity and their impact on the quantification will be presented. To analyze the effect of changing grain sizes and ratios, plasma parameters like electron temperature and electron density have been determined and compared. Additionally, for each sample the ablation rate and efficiency were calculated. Therefore, samples with defined grain sizes were made and analyzed using LIBS. The grain size distributions were analyzed with x-ray diffraction (XRD). The used LIBS system operates with a low energy NdCr:YAG laser (pulse energy of 3 mJ, a wavelength of 1064 nm, a pulse width of 1.5 ns, a repetition rate of 100 Hz) and two different Czerny-Turner spectrometers (UV and NIR range). In combination with a translation stage, a two-dimensional evaluation of the concrete heterogeneity is possible. For the objective and automated evaluation, multivariate cluster algorithms are used

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## Fractionation and speciation analysis of manganese in wheat samples

Emilia Grygo-Szymanko<sup>A\*</sup>, Anna Telk<sup>A</sup>, Danuta Dudek-Adamska<sup>A</sup>,

Natalia Miliszkiewicz<sup>A</sup>, Stanisław Walas<sup>A</sup>

<sup>A</sup> Department of Analytical Chemistry, Jagiellonian University in Krakow, Krakow, Poland

\*emilia.grygo@doctoral.uj.edu.pl

**ABSTRACT:** Manganese is a trace element essential for the proper functioning of all living organisms. In plants, manganese playing important role during the process of photosynthesis, by acting as a catalytic center of photosystem II [1]. Moreover, manganese is a cofactor for many enzymes (such as superoxide dismutase, isocitrate dehydrogenase or the pyruvate carboxylase) [2]. Plants absorb manganese(II), and its transport is enabled due to the formation of complexes with carriers such as proteins (AtIRT1, Nramp, PHO84, AtYSL) and amino acids (nikotiamine, glutathione, serine, glycine) [3]. The excess of manganese is accumulated mainly in the juice cell of vacuole, but it may also be deposited in the cell wall or chloroplasts, depending on the plant species [4]. Studies have shown that manganese is one of the factors causing oxidative stress in plants [5,6], hence the knowledge of manganese speciation could give valuable information on the toxicity of selected forms. In speciation analysis, sample preparation plays important role, in particular due to the problems with the stability of species, and it is primarily related to the matrices of samples and chosen technique of analysis. Presented results relate to various aspects of plant samples preparation (e.g. Triticum L.) for determination of manganese species by chromatographic techniques coupled to inductively coupled plasma mass spectrometry (ICP-MS). Preparation of wheat samples including the choice of reagent for manganese extraction ensuring the highest efficiency of this process was investigated. The extraction efficiency of manganese from plant material was calculated as the ratio of manganese concentration determined using ICP-MS in extracts and samples digest with the use of microwave system. Simultaneously fresh, dry, freeze-dry and freeze samples were evaluated. Other parameters like the extraction time, a method for purification of extracts and storage conditions were also assessed. The quality of the total procedure was controlled by manganese determination in reference material of wheat (IPW 682). Chosen extrahents allowed fractionation of manganese into water and protein manganese fractions. Speciation of manganese was carried out using high performance liquid chromatography (inter alia: ion pair chromatography, anion exchange chromatography) with ICP-MS. Acknowledgment: The research was financed by the National Science Centre, Poland, project no. 2013/11/D/ST4/02839.

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## Analyses of multielemental thin films via laser-induced breakdown spectroscopy

Emanuel Axente<sup>A</sup>, Jörg Hermann<sup>\*B</sup>, Gabriel Socol<sup>A</sup>, Valentin Craciun<sup>A</sup>

<sup>A</sup>Laser-Surface-Plasma Interactions Laboratory, National Institute for Lasers, Plasma and Radiation Physics, 409 Atomistilor Street Magurele, Romania;

<sup>B</sup>LP3, CNRS/Aix-Marseille Université, 163 av. Luminy, 13288 Marseille, France.

\*hermann@lp3.univ-mrs.fr

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*ABSTRACT: Thin (<1  $\mu\text{m}$ ) and very thin (<100 nm) film materials have already proven to be at the forefront for continued advances in several emerging cutting edge technologies. Among these, challenging applications are under development in the fields of energy storage, thermoelectrics, photovoltaics, nanoelectronics, hard coatings and smart biomaterials. Consequently, better techniques are required for the precise and accurate measurements of the structure and the elemental composition of thin films. Indeed, with decreasing film thickness, traditional measurement methods suffer from low accuracy as a result of limited depth resolution. Thus, very few techniques such as Rutherford backscattering are recognized to enable accurate compositional analyses of thin films. Other techniques, that are well established for elemental analysis of bulk materials, suffer from difficulties of measurement calibration. Therefore, calibration-free laser-induced breakdown spectroscopy appears as a promising solution to overcome these difficulties. Here we report on LIBS analyses of thin films based on plasma modeling. The measurement concern relative simple bi-elemental films, and also complex multielemental coatings produced by pulsed laser deposition. The results are compared to those obtained with standard-less complementary measurements using energy-dispersive X-ray spectroscopy (low accuracy) and Rutherford backscattering spectrometry (high accuracy). The influences of the experimental conditions and the accuracy of available spectroscopic data on the analytical results are discussed.*

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## Investigation of surface contamination by aluminum on classically-manufactured fused silica windows.

Christoph Gerhard<sup>\*A</sup>, Olivier Uteza<sup>B</sup>, Jörg Hermann<sup>B</sup>

<sup>A</sup>Faculty of Natural Sciences and Technology, University of Applied Sciences and Arts, Göttingen, Germany;

<sup>B</sup>LP3, CNRS - Aix-Marseille University, Marseille, France.

\*christoph.gerhard@hawk-hhg.de

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**ABSTRACT:** *The surface uniformity of optical properties of classically-manufactured glass surfaces may have a considerable impact on the final functionality of an optical component. Against this background, the grade and distribution of surface contamination by working materials used during classical manufacturing such as lubricants, lapping suspensions and polishing agents are of specific interest. For instance, residues from such substances can lead to a decrease in the laser-induced damage threshold or locally modify the characteristics and performance of applied coatings. The distribution of surface and sub-surface contamination by aluminum, a well-established lapping and polishing agent, on classically-manufactured circular fused silica samples was investigated by laser-induced breakdown spectroscopy in the present work. It is shown that nearly no aluminum was found at the center of these samples whereas considerable contamination was detected close to the sample borders. In-depth measurements revealed that the penetration depth of aluminum contamination amounts to some tens of microns for the border region. In addition to LIBS measurements, the surface uniformity was evaluated regarding surface roughness and index of refraction by atomic force microscopy and ellipsometry. It was ascertained that the surface roughness was about two times larger at the center region than at the border. Moreover, the index of refraction increases from the center towards the border. These results are in good agreement with the distribution of aluminum as measured via laser-induced breakdown spectroscopy and indicate a non-uniform impact of the tools used during manufacturing on the glass surface in a locally selective manner. The findings may be of specific interest for different applications and especially for the realization of large-scale dielectric coatings.*

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## Raman light scattering and infrared absorption studies of the phase transition and reorientational dynamics of H<sub>2</sub>O ligands and ReO<sub>4</sub><sup>-</sup> anions in [Mg(H<sub>2</sub>O)<sub>4</sub>](ReO<sub>4</sub>)<sub>2</sub>.

Joanna Hetmańczyk<sup>\*A</sup>, Łukasz Hetmańczyk<sup>A</sup>, Anna Migdał-Mikuli<sup>A</sup>

<sup>A</sup>Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060, Kraków, Poland

\*joanna.hetmanczyk@uj.edu.pl

**ABSTRACT:** At room temperature tetraaquamagnesium perrhenate crystallizes in a triclinic crystal system, within the space group No. 2 = P-1, with one molecule in the unit cell. The following unit cell constants:  $a = 6.4730(7) \text{ \AA}$ ,  $b = 7.0307(8) \text{ \AA}$ ,  $c = 7.3330(8) \text{ \AA}$ ,  $\alpha = 64.3676(19)^\circ$ ,  $\beta = 70.215(2)^\circ$ ,  $\gamma = 71.684(2)^\circ$  were determined by us. These values agree very well with literature data [1]. The magnesium atoms in this structure are surrounded by four oxygen atoms from water molecules and by two oxygen atoms from perrhenate anions in a slightly distorted octahedral arrangement with an average Mg-O distance of  $\sim 2.04 \text{ \AA}$ . The ReO<sub>4</sub><sup>-</sup> anions have a mostly regular tetrahedral geometry with an average Re-O bond length of  $1.730 \text{ \AA}$ . The polymorphism of the [Mg(H<sub>2</sub>O)<sub>4</sub>](ReO<sub>4</sub>)<sub>2</sub> compound was investigated for the first time by us by means of differential scanning calorimetry (DSC). The measurements were performed in the temperature range of 295-120 K on cooling and heating of the sample at different rates. One reversible phase transition of the investigated compound has been found at:  $T_c^h = 285.1 \text{ K}$  (onset on heating) and  $T_c^c = 256.5 \text{ K}$  (onset on cooling). The large thermal hysteresis of the phase transition temperature  $T_c$  equal to ca.  $28.6 \text{ K}$  and the heat flow anomaly sharpness suggest that the detected phase transition is a first-order one. The moderate entropy change ( $\Delta S \approx 4.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) connected with observed phase transition indicates some kind of dynamical disorder. X-ray single crystal measurements revealed that crystal structure of the low temperature phase does not change significantly. The crystal structure at 100 K is nearly the same as that at 298 K. The space group (P-1, No.2) is the same for high and low temperature phase. However, small changes in water molecule orientation and changes in the hydrogen bond network are clearly visible. Dynamics of water molecules was probed by infrared (FT-FIR, FT-MIR), Raman light scattering (FT-RS) and inelastic neutron scattering (INS) spectroscopies. The neutron scattering (INS) studies were conducted with NERA [2] time of flight spectrometer (Dubna in Russia) in the temperature range of 9–295 K. Vibrational spectroscopy measurements were performed in order to establish relationship between the observed phase transition and reorientational motions of the H<sub>2</sub>O ligands. In case of FT-IR and FT-RS data we observed splitting as well as narrowing of some bands connected with H<sub>2</sub>O vibrations in the vicinity of phase transition. The density functional theory plane wave calculations of the normal modes within the periodic boundary conditions (CASTEP code [3]) were also performed in order to support band assignment. We have obtained good agreement between calculated and experimental data (IR, RS and INS spectra).

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## Rapid and Continuous Analysis Method for Steel Pickling Solution Using Near-Infrared Spectroscopy

Masao Inose<sup>\*A</sup>, Tomohiro Matsushima<sup>B</sup>, Satoshi Kinoshiro<sup>A</sup>, Kazunori Tahara<sup>C</sup>, Shigeyuki Aizawa<sup>D</sup>,  
Hideko Tanaka<sup>E</sup>, Toshiki Ohara<sup>E</sup>

<sup>A</sup>Steel Research Laboratory, JFE Steel Corp., Kanagawa, Japan; <sup>B</sup>Functional Materials Solution Division, JFE Techno-Research Corp., Chiba, Japan; <sup>C</sup>East Japan Works, JFE Steel Corp., Chiba, Japan; <sup>D</sup>JFE Steel Galvanizing(Thailand) Ltd., Rayong, Thailand; <sup>E</sup>Yokogawa Electric Corp.; Tokyo, Japan

\*m-inose@jfe-steel.co.jp

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**ABSTRACT:** In the production of steel sheet, the surface of the steel is inevitably oxidized. Removal of this oxide layer, by acid pickling, is required. Controlling the acid concentration in the pickling process is of primary importance for maintaining product quality. However, due to the increase in line speed, the acid concentration of the pickling solution changes dramatically in short time periods. This makes it difficult for conventional chemical analysis to catch up with the changes of concentration. Currently, near-infrared spectroscopy (NIR) is attracting attention as a rapid analytical method for determining the concentration of solutions. Therefore, the near-infrared spectroscopy (NIR) was applied as a rapid analysis method to measure the concentrations of acid and iron in acid pickling solutions. The results of experiments revealed that the concentrations of acid and iron can be calculated by multivariate analysis by using the measured spectra of solutions containing varied amounts of acid and iron ions. An actual pickling line test was performed, and a good correlation between the NIR results and the chemical analysis values was obtained. It was also found that long-term continuous measurement is possible by utilizing this system.

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## Nuclear Forensics Utilizing Machine Learning Enabled Peak-Free LIBS and LAMIS

\*Angeyo Hudson Kalambuka<sup>A</sup>, Bobby Bhatt<sup>A</sup>, Alix Dehayem<sup>A</sup>, Joy Namachanja<sup>B</sup>, Bernard Wanyonyi<sup>C</sup>

<sup>A</sup>Department of Physics, University of Nairobi, P.O. Box 30197 Nairobi, Kenya; <sup>B</sup>Department of Chemistry, University of Nairobi, P. O. Box 30197 Nairobi, Kenya; <sup>C</sup>Institute of Nuclear Science & Technology, University of Nairobi, P.O Box 30197 Nairobi, Kenya.

\*hkalambuka@uonbi.ac.ke

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**ABSTRACT:** As a result of the global nuclear renaissance there is growing danger of nuclear proliferation, complicated further by possibilities for terrorism utilizing improvised nuclear devices (IND) and/ radiological dispersal devices (RDD). This places a critical challenge on the existing nuclear forensics (NF) analysis techniques with regard to coping with tasks that demand rapid, direct, and minimally-invasive characterization of nuclear and radiological materials (NRM) especially if they are of limited size and/ or are concealed (typical in nuclear forensics). LIBS is extremely attractive to perform direct, rapid and minimally invasive analysis. As the utility of LIBS in air and atmospheric pressure is limited owing to ablation-related matrix effects that result from the strongly coupled transient laser-matter interactions leading to the absence of clearly discernible analyte peaks we combine in our research group the technique with machine learning (hereby called machine learning enabled peak-free LIBS) to search for and analyze a wide variety of nuclear forensic signatures (isotopic - U, Pu, O, Pb, Sr, Nd, S) as well as chemical (rare-earth elements (REE), trace metal impurities) in NRM accruing from both the back and front end of the nuclear fuel circle. Isotopic analysis is realized via LAMIS where we exploit machine learning to remove the low resolution limitation and enable quantitative analysis. LAMIS in air and atmospheric pressure is possible as the laser plasma exhibits large isotopic splitting (which is enhanced using machine learning) due to contributions of the rotational and vibrational states of the molecule. Whilst the advantages of peak-free LIBS and LAMIS are clear, the identity and distribution of the nuclear forensic signatures in the analyzed materials does not appear in a straightforward way, owing to the interpretative challenges of high-dimensional data. This is the other reason we combine the techniques with machine learning, to enable mining (management, analysis and visualization of large data) and the extraction of information from the spectra thus providing greater versatility. This paper describes machine learning enabled peak-free LIBS and LAMIS utilizing PCA, SVM, PLS, ANN, KNN, ICA, etc. to reduce the spectral components dimension, perform pattern recognition as well as multivariate calibration of trace nuclear forensic signatures. A standard is required only at the beginning (to delineate the analyte spectral regions of interest), and the the end (for method validation). The paper further provides and discusses selected results from the nuclear forensic analysis and attribution of uranium ores, uranium-bearing minerals, 'hot' aerosols, uranium ore concentrates, uranium mine tailings, as well as nuclear waste and fuel simulates. The results highlight and demonstrate machine learning enabled peak-free LIBS and LAMIS as versatile, sensitive and rapid nuclear forensic techniques.

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## Extending the applicability of the single particle ICP-MS technique to the investigation of nanorods and nanoalloys

Ildikó Kálomista <sup>A</sup>, Albert Kéri <sup>A</sup>, Ditta Ungor <sup>B</sup>, Edit Csapó <sup>B,C</sup>, Imre Dékány <sup>B</sup>, Gábor Galbács <sup>A\*</sup>

<sup>A</sup> Department of Inorganic and Analytical Chemistry, University of Szeged, Szeged, Hungary; <sup>B</sup> MTA-SZTE Supramolecular and Nanostructured Materials Research Group, Szeged, Hungary; <sup>C</sup> Department of Physical Chemistry and Materials Sciences, University of Szeged, Szeged, Hungary.

\*galbx@chem.u-szeged.hu

**ABSTRACT:** Single Particle Inductively Coupled Plasma Mass Spectrometry (spICP-MS) emerges as a promising novel nanomaterial characterization method which offers distinct advantages over other methods, especially in the case of the investigation of aqueous nanodispersions. In this technique, the sensitive ICP-MS spectrometers are used in the time-resolved mode for the measurement of dilute nanodispersions (particle concentrations less than  $10^5 \text{ mL}^{-1}$  are adequate) via monitoring the signal from one of the constituting elements of the nanoparticles (NPs). After the statistical evaluation of the signal time profile, information can be obtained about not only the elemental (isotopic) composition of the NPs, but also their size distribution, as well as the particle concentration. The measurement is fast (takes only a couple of minutes) and the required sample volume is also small (a few mL) [1,2].

spICP-MS studies in the literature are described for spherical and monoelemental nanoparticles, for which the data evaluation is easiest and the sensitivity is highest. At the same time, modern industrial and materials science applications use, in great numbers, engineered NPs which have a large diversity in terms of their shape and composition. The reason for this is that the shape of the nanoparticles can result in different surface properties, morphology, chemistry, electrokinetics, aggregation kinetics, etc. [3]. Another group of nanomaterials in the focus of recent research is that of nanoalloys, which present very complex structures and properties, that can be tailored for specific and industrially relevant applications such as plasmonics, catalysis, data storage, etc. [4]. In spite of the practical importance of these NPs, studies dealing with the measurement of nanorods and nanoalloys in the spICP-MS literature are extremely scarce [5].

Our present work is focused on the spICP-MS measurement of nanorods and bimetallic nanoalloy particles. We found that suitable measurement conditions and data evaluation approaches actually allow the determination of not only the mass (volume) distribution or number concentration of such particles, but also their estimated aspect ratio (in case of nanorods) and structure (e.g. core-shell, homogeneous, hollow, etc.). Our contribution will present data for gold nanorods and gold-silver spherical nanoalloys, specifically synthesized for this study, obtained by using both regular (millisecond-range) and high (microsecond-range) time resolution spICP-MS experiments. Special attention is paid to the problems of optimization and calibration.

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## Raman Spectroscopic and Theoretical Study of Liquid and Solid Water within the Spectral Region 1600–2300 cm<sup>-1</sup>

G.A. Pitsevich<sup>A</sup>, I.Yu. Doroshenko<sup>B</sup>, E.N. Kozlovskaya<sup>A</sup>, A.D. Leshchenko<sup>A</sup>, A.A. Kamnev\*<sup>C</sup>

<sup>A</sup>Belarusian State University, Nezavisimosti Ave., 4, 220030, Minsk, Belarus; <sup>B</sup>Taras Shevchenko National University of Kyiv, Volodymyrska Str., 64/13, 01601, Kyiv, Ukraine; <sup>C</sup>Institute of Biochemistry and Physiology of Plants and Microorganisms, Russian Academy of Sciences, 13 Prosp. Entuziastov, 410049, Saratov, Russia

\* aakamnev@ibppm.ru, a.a.kamnev@mail.ru (A.A. Kamnev)

**ABSTRACT:** Determination of the local structure of water in the liquid state is a topical problem nowadays. Although 80 years ago Cross et al. (JACS 59 (1937) 1134) for the first time noted an anomalously high intensity of the line at 2170 cm<sup>-1</sup> interpreted as a combined bending and librational vibration, and later a number of reports on Raman spectra of water and ice have increased rapidly, it can be stated that unusual properties of the Raman line at 2170 cm<sup>-1</sup> have not been studied. In this work, liquid deionised and triply distilled water was used in our experimental spectroscopic investigations. Raman spectra were recorded using an FT-Raman MultiRam Bruker spectrometer with a 785 nm laser (500 mW) and a Silicone Avalanche diode as a detector. Thermostabilisation during temperature investigations was provided by a LINKAM cryostat (model FTIR 600). Spectra were recorded in the spectral range from 50 to 5000 cm<sup>-1</sup> with an optical resolution of 0.5 cm<sup>-1</sup>. Water in the liquid phase is a mixture of high density liquid (HDL) and low density liquid (LDL) with the ratio 3:1. The local structure of LDL is close to the crystal structure of water at normal conditions, when each molecule is surrounded by four molecules, which are located in vertices of a tetrahedron, and is connected to them by four hydrogen bonds. In HDL, the tetrahedral structure of the nearest environment is broken, and the number of H-bonds decreases to 3 or 2. In order to simulate vibrations in the two types of the local structure of water, the structure of water pentamer was optimised in the approximation B3LYP/cc-pVTZ assuming that four non-central water molecules are located in vertices of a tetrahedron. Comparing Raman spectra obtained at +3°C and -4°C one can notice that arbitrary intensities of Raman lines near 1630 and 2200 cm<sup>-1</sup> drastically change with the transition from the liquid to the solid phase. It occurs mainly because of the intensity decrease of the line at 1630 cm<sup>-1</sup>. This can be explained by the fact that in the crystalline phase, almost each water molecule acts as a donor for two H-bonds. It is clear qualitatively that involving a water molecule into one or two H-bonds as a donor should increase the bending vibration frequency and decrease the intensity of the corresponding Raman line owing to a decrease in the amplitude of this vibration. Basing on the ratio HDL:LDL=3:1 and assuming that LDL corresponds to water molecules with two H-bonds, we varied the ratio between the number of molecules with one and those without donor H-bonds, keeping the portion of water molecules with two donor bonds fixed (0.25) in order to find the best agreement of the calculated and experimental contours of the corresponding Raman lines in the liquid phase. In the crystalline phase, the tetrahedral structure dominates; therefore the portion of water molecules with one and without any donor H-bonds was set ≤ 2%. According to calculations, an increase in the number of donor H-bonds leads to a frequency increase of the bending vibrations, but the Raman activity of these vibrations has an opposite dependence. Simulation of the experimentally observed Raman contours of the bending vibrations in the liquid and solid states is in good agreement with the assumption that the portion of molecules involved in double donor H-bonding increases from 0.25 to almost 1 with the transition from the liquid to the crystalline phase. Calculations of frequencies and intensities of the combined rocking-bending vibration have shown the possibility of a slight weakening of the H-bond in the excited state owing to a large amplitude of the corresponding vibration. However, in general, the model of water pentamer cannot adequately explain the experimentally observed parity of intensities of the Raman lines assigned to the bending and combined vibrations near 2200 cm<sup>-1</sup>. Probably, this phenomenon can be explained by collectivity of the corresponding vibrations in a crystal.



## Easy Determination of Chromium and Arsenic Species in Toys and Food using hyphenated LC-ICPMS technique applying the new developed Shimadzu Time Resolved Measurement Software

Jan Knoop<sup>\*A</sup>, Jürgen Schram<sup>B</sup>, Davide Pasina<sup>C</sup>, Uwe Oppermann<sup>A</sup>, Sebastian Szopa<sup>D</sup>, Nils Garnebode<sup>E</sup>

<sup>A</sup>Shimadzu Europa GmbH, Duisburg, Germany; <sup>B</sup>Faculty of Chemistry, Niederrhein University of Applied Science, Krefeld, Germany; <sup>C</sup>Shimadzu Italia SRL, Milano, Italy; <sup>D</sup>Shim-Pol, Izabalín, Poland; <sup>E</sup>Shimadzu Deutschland GmbH, Duisburg, Germany

\*jkn@shimadzu.eu

**ABSTRACT:** The importance to determine not the total element concentration but the species concentration within several applications like in industry and food sector is increasing from year to year. The reason is that from point of toxicity the information about species concentration is more relevant than the total elemental concentration. For example DIN EN 71-3 requires to determine the migration of Chromium (III) and Chromium (VI) from toy materials<sup>[1]</sup>. The different specified maximum migration limits for these species give a direct connection to the toxicity, which is for one of the categories of toy material for example 9,4 mg/kg for Cr(III) and only 0,005 mg/kg for Cr(VI). The most typical way now is to determine the total Chromium. If the migration is below 0,005 mg/kg the toy is in accordance to DIN EN 71-3, but if the amount of migrated Chromium is higher, speciation analysis needs to take place. Within this poster the ICPMS Time Resolved Measurement Software developed by Shimadzu is applied, enabling the control of both devices (LC and ICPMS) within the same software platform and as a consequence a much more easy use of hyphenated techniques. Further application example is the Arsenic speciation in rice, which is getting more relevant because of the tendency that an increasing amount of people follow gluten free diets (even without having celiac disease) and different products of rice like rice flour are a common substitute of wheat products. As rice is well known to bioaccumulate certain toxic elements like arsenic, special attention has to be paid to avoid that any negative consequences for the human health are avoided.

[1] DIN EN 71-3:2014: Safety of toys – Part 3: Migration of certain elements.



## Two-step Laser Excitation of Triplet Rydberg States of Mg Atom from the $3s3p\ ^3P_0^O$ metastable state

Yuto Kobune<sup>A</sup>, T. Amemiya<sup>A</sup>, H. Ito<sup>A</sup>, K. Yamane<sup>B</sup>, K. Kitano<sup>A</sup>, Y. Mizugai<sup>B</sup>, and H. Maeda<sup>A\*</sup>

<sup>A</sup>Dept. of Sci. & Eng., Aoyama Gakuin Univ., 5-10-1 Fuchinobe, Sagamihara, Kanagawa 252-5258, Japan; <sup>B</sup>Dept. of Sci. & Eng., Sophia Univ., 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan

kobu.0921@gmail.com, hmaeda@phys.aoyama.ac.jp

**ABSTRACT:** Providing spectroscopic data of neutral magnesium (Mg) atom is intrinsically important for further progress of atomic physics and astrophysics [1]. In the present study we have made laser spectroscopy of  $3snp$  ( $26 \leq n \leq 59$ )  $^3P_{0,1,2}$  Rydberg states of Mg atom for the first time, to our knowledge, by a two-step resonant excitation of Mg in the  $3s3p\ ^3P_0^O$  metastable state. In our experiment metastable atom beam of Mg is produced via laser ablation of a Mg rod in a vacuum chamber, of which the background pressure is on the order of  $10^{-4}$  Pa. Laser ablation of the Mg rod has been done between a pair of low voltage ( $\sim 200$  V) electrodes so that a charged component in the ablation plume initiates discharge between the electrodes [2]. This ablation-initiated discharge brings a certain amount of Mg atoms into the  $3s3p\ ^3P_0^O$  metastable state, which is the lowest excited state lying  $21850.405\text{ cm}^{-1}$  above the  $3s^2\ ^1S_0$  ground state [3]. Magnesium atoms in the  $3s3p\ ^3P_0^O$  metastable state are then resonantly excited into Rydberg states via  $3s4s\ ^3S_1$  intermediate state at  $41197.403\text{ cm}^{-1}$  [3] using two sets of home-made Littman-Metcalf type tunable dye lasers pumped by a 20-Hz Q-switch Nd:YAG laser. Typical spectral linewidth of our dye lasers are around  $0.3\text{ cm}^{-1}$ . Atoms excited into Rydberg states are field-ionized by applying pulsed electric field and detected using a dual micro-channel-plate detector. Wavelength calibration of excitation laser has been done by recording interference fringes from a solid or an air-spaced etalon and optogalvanic signal from an argon hollow-cathode lamp at the same time. In our measurements, a single Rydberg series has been identified which is assigned as  $3snp\ ^3P$  Rydberg series in accordance with the electric dipole selection rules. We note that  $J = 0 - 2$  fine-structures of the  $3snp\ ^3P$  states cannot be resolved due probably to the broad line width of the excitation laser [4].

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## Monitoring dynamic electrochemical processes with in-situ ptychography and keyhole CDI

George Kourousias<sup>\*A</sup>, Benedetto Bozzini<sup>B</sup>, Michael Jones<sup>C</sup>, Grant Van Riessen<sup>D</sup>, Maya Kiskinova<sup>A</sup>,  
Alessandra Gianoncelli<sup>A</sup>

<sup>A</sup> Elettra-Sincrotrone Trieste, Basovizza, Trieste, Italy; <sup>B</sup> Department of Engineering, Salento University, Lecce - Monteroni, Italy; <sup>C</sup> Faculty of Health and Institute of Health and Biomedical Innovation, Queensland University of Technology, Brisbane, Australia; <sup>D</sup> La Trobe Institute for Molecular Science, La Trobe University, Melbourne, Australia

\*george.kourousias@elettra.eu

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**ABSTRACT:** *The presentation reports on novel Soft X-ray Fresnel CDI ptychography results, demonstrating the potential of this method for dynamic studies. Our in-situ ptychography experiments explored the electrodeposition process of Mn and Co/polypyrrole (PPy) nanocomposites, Pt-free candidates for fuel cell catalysts [1]. The measurements were performed using a custom-made three-electrode microcell [2]. The cell has been developed at the TwinMic beamline of Elettra during a series of experiments that were continued at the SXRI beamline of the Australian Synchrotron [1]. The ptychography-based investigation of the electrodeposition dynamics was executed during the in-situ electrical biasing of the electrochemical cell. Besides the observation of morphological changes, we retrieved the spectroscopic information, provided by multiple ptychographic energy scans across Mn and Co edges. The most important issues related to the computational aspects of such experiments will be outlined and potential improvements of the methodology will also be discussed.*

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## Development of HPLC Species-Specific / Unspecific ID ICP MS Method for the Determination of Selenium Species

Agnieszka Anna Krata<sup>A\*</sup>, Ewa Bulska<sup>A</sup>, Jakub Karasinski<sup>A</sup>, Marcin Wojciechowski<sup>A</sup>

<sup>A</sup>Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, Zwirki i Wigury 101, Warsaw, 02-089, Poland

\*kratka@chem.uw.edu.pl

**ABSTRACT:** Speciation analysis is defined as a process assuring the separation and quantification of different chemical forms, in which element of interest can be present in a sample. The commonly used approach for the speciation studies combine the separation of the species present in a given object by chromatographic methods followed by the measurement of the element content by any of the element specific atomic spectrometry techniques. The ability to perform isotope ratio measurements and as a consequence isotope dilution (ID) analysis plays a key role in HPLC ICP MS technique. This modification has a great potential, particularly for the quantitative determination of speciation forms of elements. The main assumption of isotopic dilution method is based on the measurement of isotope ratios in a sample, where its isotopic composition has been altered by the addition of a known amount of an isotopically enriched standard of the element of interest. The aim of this study was to optimize the measurement procedure of isotope dilution mass spectrometry technique in a species-specific mode of the element and species-unspecific mode in order to quantify the concentration of selenomethionine in plant samples. The species specific IDMS procedure requires the use of a spike solution containing the species to be analyzed in an isotopically labelled form. The spike solution is added to the sample at the very beginning of the analytical procedure, and once complete mixing between the added enriched species and the naturally occurring, the sample is ready for measurements, thus all traditional advantages of isotope dilution analysis can be fully exploited. However, it needs to be stressed that this mode is limited by the lack of commercial species-specific enriched spikes. Thus the second approach is based on the use of the species-unspecific spiking mode. The addition of the external isotope is carried out after the complete separation of the naturally occurring species in the sample. The spike and reference solution may be composed of a chemical form different from that of the species originally present in a sample. Although this mode of spiking does not offer the full range of advantages listed before, it is still consider to be very useful in many of the applications.

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## Atomization Mechanism of Hydride Forming Elements in Heated Quartz Tube and Dielectric Barrier Discharge Atomizers

Jan Kratzer<sup>\*A</sup>, Stanislav Musil<sup>A</sup>, Milan Svoboda<sup>A</sup>, Jiří Dědina<sup>A</sup>, Zoltán Mester<sup>B</sup>, Ralph E. Sturgeon<sup>B</sup>

<sup>A</sup>Institute of Analytical Chemistry of the CAS, v. v. i., Veveří 97, 602 00 Brno, Czech Republic; <sup>B</sup>National Research Council of Canada, 1200 Montreal Road, Ottawa, Ontario K1A 0R6, Canada;

\*jkratzer@biomed.cas.cz

**ABSTRACT:** The mechanism of atomization of hydride forming elements in a novel planar dielectric barrier discharge (DBD) atomizer as well as in a conventional externally heated quartz tube atomizer (QTA) was investigated. Bismuth and selenium were selected as model analytes. A variety of spectrometric methods was employed, including atomic absorption spectrometry (AAS) to monitor distributions of free atoms along the optical path, inductively coupled plasma mass spectrometry (ICP-MS) to investigate the analyte fractions breaking through the atomizer on the one hand and being retained in the atomizer (after leaching) on the other. Direct analysis in real time (DART) coupled to an Orbitrap MS was employed to identify the structures of the species arising from the hydride generator as well as the atomizer. The effect of hydrogen on atomization was investigated by hydride generation-cryotrapping (CT)-AAS. Last, but not least, the process of selenide atomization was studied also by means of <sup>75</sup>Se radiotracer.

Free Bi atoms were essentially absent outside the central part of the DBD atomizer, whereas the fraction of free Se atoms in the same region was estimated to be ca 80% of the value observed in the middle of the atomizer. The gas phase analyte fraction transported beyond the confines of the DBD or QTA atomizers, quantified by ICP-MS, was less than 10% for Bi. On the contrary, this breakthrough estimated by ICP-MS for Se was ca 50% and 90%, respectively for DBD and QTA. The amount of Bi found in nitric acid leachates of the interiors of both atomizers was ca 90%. In the case of Se, the analyte fraction in the leachates of the atomizers reached 43% and 15%, respectively, for the DBD and QTA. Experiments with <sup>75</sup>Se radiotracer revealed that the analyte fraction breaking through the atomizers reaches 64% for the DBD and 88% for the QTA. These results are in a good agreement with those obtained by ICP-MS for Se. Combination of radiotracer and image plate autoradiography permitted visualization of the spatial distribution of Se deposits in both atomizers. In the QTA, analyte is deposited in a narrow zone at both colder ends of the optical arm (200 – 400 °C) protruding outside the heating unit. On the contrary, Se was deposited homogeneously along the whole length of the optical arm of the DBD. By use of CT experiments, the presence of hydrogen was found to be essential for atomization of both analytes in both atomizers. Results from DART-MS measurements will also be presented.

Our results clearly show different behavior of selected hydride forming elements, indicating higher reactivity of Bi free atoms compared to those of selenium. However, the atomization mechanism is likely identical for both analytes, proceeding via reactions with H radicals.

This work was supported by the Czech Science Foundation (P206/17-04329S) and Institute of Analytical Chemistry of the CAS, v. v. i. (Institutional Research Plan, project no. RVO: 68081715).

## **S<sup>2</sup>XAFS: A new experimental set-up for time-resolved X-ray absorption spectroscopy in a ‘single-shot’**

Anicó Kulow<sup>\*A,B</sup>, Ana Guilherme Buzanich<sup>A</sup>, Martin Radtke<sup>A</sup>, Uwe Reinholz<sup>A</sup>,  
Heinrich Riesemeier<sup>A</sup>, Christina Strelt<sup>B</sup>

<sup>A</sup> Federal Institute for Materials Research and Testing (BAM). Richard-Willstaetter-Straße 11, 12489 Berlin, Germany; <sup>B</sup> Institute of Atomic and Subatomic Physics, Vienna University of Technology, Stadionallee 2, 1020 Vienna, Austria

\*anico.kulow@bam.de

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*ABSTRACT: A newly developed ‘Single-shot’ X-ray Absorption Spectroscopy Fine Structure (S<sup>2</sup>XAFS) setup is presented. It enables both time- and spatially resolved EXAFS information simultaneously in a ‘single shot’. First tests of this setup were performed at the BAMline @ BESSY-II (Berlin, Germany). The principle is simple: A primary broadband beam passes through the sample and is then diffracted by a convexly bent Si (111) crystal. The resulting divergent beam is collected by an area sensitive detector. Two rotating motors are used to allow a  $\theta$ -2 $\theta$ -geometry. The bending mechanism was designed and manufactured in house. It enables an exact and reproducible bending of a commercially available Si wafer. The bending behavior of the crystal surface was investigated experimentally and via computer simulations. Tests on metal foils were performed for the adjustment and aligning of the setup, and for specific parameters, energy calibrations were done. Beside tests on metal foils, the first in situ measurements were successfully carried out.*

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## In-situ monitoring and characterization of airborne solid particles in hostile industrial environments using stand-off LIBS

T. Delgado<sup>A</sup>, D. Girón<sup>A</sup>, J. Ruiz<sup>B</sup>, L.M. Cabalín<sup>A</sup>, J.J. Laserna<sup>A\*</sup>

<sup>A</sup>Departamento de Química Analítica, Universidad de Málaga, Facultad de Ciencias, Campus de Teatinos s/n, 29071 Málaga, España; <sup>B</sup>Departamento de Física Aplicada I, Universidad de Málaga, Facultad de Ciencias, Campus de Teatinos s/n, 29071 Málaga, España

\* laserna@uma.es

**ABSTRACT:** *In this study, the analytical possibilities of in-situ detection of solid aerosols generated in a steelmaking factory, as well as the determination of their elemental composition, have been evaluated, using a stand-off LIBS analyzer able to work at distances up to 8 meters. Two modes of interaction between laser beam and airborne particles, namely single-pulse and double-pulse laser regimes, were assessed.*

*Experimental results confirmed the main source forming aerosol particles: casting powder probably removed from the slab surface during the oxycutting process of stainless steel slabs. Both elemental (Al, Ti, Li) and molecular (CaO, CaF) emission signals confirmed the presence of particles of this lubricant powder in the analyzed atmosphere. An additional identified source of particulate matter, obviously, was the steel itself being cut, since Cr emission, coming either from the steel bulk or from the oxidized steel surface, was also detected in suspension. Finally, another potential origin of Li species in the factory atmosphere was the Li-based greases for the lubrication of rollers in the continuous casting line.*

*Computed values for sampling rates from the analysis of aerosols in a region next to the oxycutting unit indicated an enhancement of the concentration of airborne particles for the case to be running the cutting process of the slabs, compared to periods with the oxycutting unit off. Likewise, double-pulse laser measurements seem to slightly improve the sampling rate values compared to those obtained in single-pulse regime. The estimation of sampling rates was conducted using a suitable data processing method based on the analysis of standard deviation of the acquired signals.*

*Field tests have proved the viability of stand-off LIBS technology for the in-situ and real-time detection of solid aerosols in industrial environments, thus becoming an analytical on-line tool for a rapid monitoring and control of particulate emissions generated in hostile scenarios.*

## Identification strategies for steel grades at high temperature using stand-off LIBS

T. Delgado<sup>A</sup>, J. Ruiz<sup>B</sup>, L.M. Cabalín<sup>A</sup>, J.J. Laserna<sup>A\*</sup>

<sup>A</sup>Departamento de Química Analítica, Universidad de Málaga, Facultad de Ciencias, Campus de Teatinos s/n, 29071 Málaga, España; <sup>B</sup>Departamento de Física Aplicada I, Universidad de Málaga, Facultad de Ciencias, Campus de Teatinos s/n, 29071 Málaga, España

\* laserna@uma.es

**ABSTRACT:** The objective of this study is the development of a method for identification of steel grades by stand-off LIBS (laser-induced breakdown spectroscopy). Measurements on steel samples have been made at a distance of 4.5 m, at elevated temperature and firing one laser shot in each fresh position of the sample surface, simulating real conditions during the continuous casting of steel in a production line.

Discrimination between different grades is based on double-pulse ablation of the scale layer formed on the surface when the steel sample is raised up to 900°C inside a furnace in contact with air. The two laser beams (collinear Nd:YAG lasers operated at 1064 nm) are focused onto the sample with a 5x beam expander, and the emitted light is collected by means of a Maksutov-Cassegrain telescope. This telescope focuses the plasma light onto an optical fiber connected to a miniaturized spectrometer fitted with a CCD detector. Both pulse energy and temporal conditions have been optimized in terms of average ablation rate, signal-to-noise ratio and signal stability. Real-time control and monitoring of the spectral intensities, in addition to statistical treatment of acquired data have been designed, in order to detect immediate changes in the chemical composition of the scale layer, revealing an expected change in the composition of the steel matrix below.

The main challenge of the present research lies in the experimental fact that the chemical composition of such a layer deviates significantly from that of the bulk material, and not in a linear and predictable way. Moreover, a complete removal of the scale layer from the surface with a single laser shot is not feasible. Therefore, quantitative analysis or calibration-based methods have to be discarded and advanced chemometric strategies for identification purposes were developed in the lab. Discriminant Function Analysis (DFA) has been chosen as an appropriate semi-quantitative statistical method for the differentiation of steel grades from the spectral information obtained from the corresponding scale layers. The statistical parameters derived from DFA and discriminant functions are presented with good correlation values.



## Elemental profiling of wear resistant coatings by laser induced breakdown spectroscopy and energy dispersive X-ray spectroscopy

V.N. Lednev<sup>\*A,B</sup>, P.A. Sdvizhensky<sup>B</sup>, M.Ya. Grishin<sup>A,C</sup>, A.N. Fedorov<sup>A</sup>, S.M. Pershin<sup>A</sup>, Tretyakov R.S.,<sup>D</sup> Staverty A.Ya.<sup>D</sup>

<sup>A</sup> Prokhorov General Physics Institute, Russian Academy of Sciences, Moscow, Russia; <sup>B</sup> National University of Science and Technology MISIS, Moscow, Russia; <sup>C</sup> Moscow Institute of Physics and Technology (State University), Dolgoprudny, Russia; <sup>D</sup> Bauman Moscow State Technical University, Moscow, Russia

\*vasilylednev@gmail.com

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*ABSTRACT: High wear resistant coatings were analyzed by laser induced breakdown spectroscopy (LIBS) and energy dispersive X-ray (EDX) spectroscopy. Coaxial laser cladding technique was utilized to produce tungsten carbide coatings deposited on low alloy steel substrate. EDX and LIBS techniques were used for elemental profiling of major components (Ni, W, C, Fe, etc.) in the coating. A good correlation between EDX and LIBS data was observed while LIBS provided additional information on light element distribution (C, B, Si). A non-uniform distribution of WC grains along coating depth was detected by both LIBS and EDX. In contrast, horizontal elemental profiling showed a uniform tungsten carbide particles distribution. Depth elemental profiling by layer-by-layer LIBS analysis was demonstrated to be an effective method for studying tungsten carbide grains distribution in wear resistant coating without any sample preparation.*

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## Laser Crater Enhanced Raman Spectroscopy

V.N. Lednev<sup>\*A</sup>, P.A. Sdvizhenskii<sup>A</sup>, M.Ya. Grishin<sup>B,C</sup>, S.M.Pershin<sup>B</sup>

<sup>A</sup>National University of Science and Technology MISIS, Moscow, Russia; <sup>B</sup>Prokhorov General Physics Institute, Russian Academy of Sciences, Moscow, Russia; <sup>C</sup>Moscow Institute of Physics and Technology (State University), Dolgoprudny, Russia.

\*vasilylednev@gmail.com

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*ABSTRACT: Raman signal enhancement by multiple scattering inside laser crater cones was observed for the first time. Laser crater enhanced Raman spectroscopy (LCERS) yielded a 14-fold increase in the Raman spectra bands due to efficient multiple scattering of laser irradiation within the laser crater walls. The same pulsed Nd:YAG laser (532 nm, 10 ns) was used for both laser crater formation and Raman scattering experiments by varying the output pulse energy. First, powerful pulses are used to produce the laser crater and then low energy pulses are used to perform Raman scattering measurements. The laser crater profile and its alignment with the laser beam waist were found to be the key parameters for the optimization of the Raman bands intensity enhancement. Raman intensity enhancement resulted from increased surface scattering area at the crater walls rather than spatially offset Raman scattering. The increased signal-to-noise ratio resulted in limits of detection improvement for quantitative analysis using LCERS. The simplicity of instrumentation and lack of need for an optics arrangement (the same optics is used for ablation and Raman scattering measurements) make the LCERS technique a prospective tool for express quantitative analysis of powder samples including remote sensing applications.*

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## Study for Elements Determination for Evaluating their Availability in Coal and Ashes using Experimental Design and the ICP-MS Technique

Sandra Maria Maia<sup>A\*</sup>, Wolfgang Kalkreuth<sup>B</sup>, Marco F. Ferrão<sup>A</sup>, Rafaela Lorenzini<sup>A</sup>

<sup>A</sup>Instituto de Química, UFRGS, Avenida Bento Gonçalves 9500, 91501-970, Brazil; <sup>B</sup>Instituto de Geociências, UFRGS, Avenida Bento Gonçalves 9500, 91540-000, Brazil

\*sandramaia@iq.ufrgs.br

**ABSTRACT:** The coal combustion in a power plant produces bottom and fly ashes and usually these combustion residues are improperly stored at the plant site or on-site disposal. As a consequence an environmental contamination can be produced. The determination of leaching inorganic pollutant in solid waste, such as coal and ash is an important topic for further industrial applications and solid waste management. Environmental contamination caused by coal ash disposal and also their further industrial application requires the knowledge of their total metal concentration besides the available metal fraction to other environmental compartments.<sup>1</sup> In the literature<sup>2</sup> is reported the use of EDTA as a leaching agent to predict solid waste metal availability. The objective of this work was to evaluate the availability of As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, V and Zn in coal and ashes produced by coal power plants from the south of Brazil and to predict probable elements which might contribute to the environmental contamination. The total elements concentration in coal and ashes were determined by the ICP-MS technique, after acid decomposition in microwave oven and metal block for coals and ashes, respectively. For this purpose a preliminary study was made to investigate the optimal extraction conditions, considering the influence of factors such as EDTA concentration, sample mass and contact time. For the experiments one coal sample from Candiota power plant was used. For this study an experimental design was applied and the response surface methodology. By using central composite design (CCD) method, 17 experiments (including 3 repetitions at the central point) were designed. According to the results the compromise conditions (0.05 mol L<sup>-1</sup> EDTA, 1 g and 60 min) were chosen for the samples extraction. The samples were weighed in 50 mL polypropylene flasks, 20 mL of 0.05 mol L<sup>-1</sup> EDTA was added and after 60 min agitation, the samples stayed overnight. After centrifuge (35min at 3000 rpm) the supernatants were taken and diluted with 0.01mol L<sup>-1</sup> HNO<sub>3</sub>, for the analyses by ICP-MS using external calibration. With the values of the available concentrations of the elements investigated was possible to determine their available percent dividing these values by the total concentration in the samples and multiplying by 100. The mean values of available percent obtained for each element in 8 coal samples of Candiota power place showed that their availability follow the sequence Mn > Co > Cu > Pb > Ni > Zn > Cd > V > As > Cr. The methodology was also applied for ashes samples but for some elements, like Zn, matrix interferences were observed. The use of an internal standard to compensate matrix effects and standard addition calibration will be investigated in order to minimize these interferences.

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## Mercury analysis in Coal, Ash and Slag using Cold Vapor-ICPOES, After microwave digestion.

Ciro Márquez<sup>A</sup>, Mónica Antunez<sup>A</sup>, Brian Garrido<sup>A</sup>, Javier Canales<sup>A</sup>

<sup>A</sup>Facultad de Química, Departamento de Ingeniería Metalúrgica, Universidad Nacional Autónoma de México, Ciudad Universitaria, CP. 04510, Ciudad de México, México.

ciromh@hotmail.com

**ABSTRACT:** The mercury is a highly toxic element, its effects have been exposed in different forums and in specific in the Minamata Agreement (1). The Mercury presence in the environment has different anthropogenic origins. Its control is of vital importance and it is necessary to know the emission levels of the possible sources of contamination. The mercury cycle involves a variety of sources and complex processes of transport and mobilization. It is estimated that 30% of the current emissions into the atmosphere are of anthropogenic origin, while 10% come from natural sources and the rest 60% comes from re-emissions of mercury deposited and accumulated historically in soils and Oceans "(Minamata Agreement)(1) . Therefore, it is very important to have adequate analytical methods for analysis in different matrices. In the process of generating electric energy from coal, large amounts of coal are consumed and two by-products are generated; Ash and slag, which may contain mercury. Coal is difficult to analyze due to its nature, in some cases due to inorganic components that accompany it, among which are silicates(2). In the case of ash and slag, their matrix is very complex because they contain large amounts of silicates. It is possible that in these by-products the mercury present in the coal used for combustion is fixed. In this work we show an analytical method for mercury analysis at trace level in carbon, ash and slag. The used technique for all samples was microwave digestion (TITAN MPS Perkin Elmer and after, for analysis, inductively Coupled Plasma Optical Emission Spectroscopy and Cold vapor (ICP OES-CV). After different tests it was obtained a good digestion for all samples, using HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HF (5:5:2 ml) respectively. The same digestion conditions were established for the three types of samples. We used three different mercury wavelengths ( $\lambda=253.652\text{nm}$ ,  $\lambda=194.168\text{nm}$  y  $\lambda=184.886\text{nm}$ ). It was tested NaBH<sub>4</sub> and SnCl<sub>2</sub>, with KMnO<sub>4</sub> addition until purple permanent color. 0.3 g of sample weight was used and brought to 50 ml of final volume, with ASTM Type I water. The limit of detection was 40 mg / kg. NIST1635a was used to validate the method. The values obtained are in the range of 200-500 mg / kg for Coal and 311-350 mg / kg and 356-400 mg / kg for the slag and ash respectively.

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## Selective Hydride Generation of Inorganic Arsenic for Fast Screening of Samples of Marine Origin

Stanislav Musil<sup>\*A</sup>, Karel Marschner<sup>A,B</sup>, Tomáš Matoušek<sup>A</sup>, Jiří Dědina<sup>A</sup>

<sup>A</sup>Institute of Analytical Chemistry of the CAS, v. v. i., Veveří 97, 602 00 Brno, Czech Republic.

<sup>B</sup>Department of Analytical Chemistry, Charles University, Albertov 8, 128 43 Prague, Czech Republic.

\*stanomusil@biomed.cas.cz

**ABSTRACT:** Due to the much higher toxicity of inorganic arsenic (iAs) in comparison to the other organically bound As species, only iAs needs to be monitored in food. The most common approaches to speciation analysis of iAs are based on liquid chromatography coupled to element specific detector after a microwave assisted extraction using diluted acids and hydrogen peroxide. However, the approaches based on liquid chromatography do not have to fit to routine laboratories due to time demands per sample and more complicated data treatment, which makes the validation more difficult. Therefore, the development of simple and fast analytical methods is still necessary with a focus on screening of large number of samples. Recently, a method of selective hydride generation-inductively coupled plasma mass spectrometry (HG-ICP-MS) for the fast determination of iAs in rice samples was published [1] and successfully validated [2]. The method uses high concentrations of HCl (5M) and NaBH<sub>4</sub> (2%) for the selective generation of AsH<sub>3</sub> which is formed with only a minor contribution of dimethylarsane from dimethylarsinate (DMAs<sup>V</sup>). Methylarsonate (MAs<sup>V</sup>) forming methylarsane was a more pronounced interferent in iAs determination but since MAs<sup>V</sup> is generally absent or only present in trace amounts in rice, this was shown not to affect the accurate quantification of iAs. The aim of this work was to apply this method also for the samples of marine origin (fish and seaweed) whose matrix and arsenic speciation is far more complex. HCl and HClO<sub>4</sub> were tested as acids and optimized for selective HG of iAs with respect to potential interferences from MAs<sup>V</sup> and DMAs<sup>V</sup>. Addition of Antifoam B to NaBH<sub>4</sub> solution was investigated to deal with excessive foaming of extracts (by 2% HNO<sub>3</sub> and 3% H<sub>2</sub>O<sub>2</sub>) given by high protein content. The method was applied to certified reference materials from National Research Council Canada – DORM-3, DORM-4, TORT-3, DOLT-4, DOLT-5, PRON-1 and SQID-1 and to four seaweed samples. Comparative analyses were performed with postcolumn HG-atomic fluorescence spectrometry [3]. The method of selective HG-ICP-MS is sensitive and can be used as the fast screening method for iAs in large sample sets. It is fully automated using a standard ICP-MS autosampler with analysis time just over 4 minutes per sample.

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## Spectroscopic study of peculiarities of mercury distribution in coals

Nikolay Mashyanov <sup>\*A</sup>, Sergey Pogarev <sup>A</sup>, Elena Panova <sup>A</sup>, Sergey Sholupov <sup>B</sup>, Nikolay Panichev <sup>C</sup>,  
Mpho Mathebula <sup>C</sup>, Vladimir Ryzhov <sup>D</sup>

<sup>A</sup> St. Petersburg State University, St. Petersburg, Russia, <sup>B</sup> Lumex-marketing LLC, St. Petersburg, Russia, <sup>C</sup> Tshwane University of Technology, Pretoria, Republic of South Africa, <sup>D</sup> Lumex Analytics GmbH, Wakendorf, Germany

\*nrm@lumex.ru

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**ABSTRACT:** Coal is apt to concentrate many toxic elements whose content is governed by geological and geochemical specificity of the coal deposit. Serious environmental concern is being associated with the presence of mercury in coal. The mercury concentration in coal varies by more than 5 orders of magnitude, from less than 1 ppb to 300 ppm. Mercury species in coal can be represented by elemental mercury, syngenetic mercury, initially bound to organic matrix, isomorphic in sulfides, and to silica (mainly clay) minerals. The peculiarities of mercury distribution in coal have been studied by thermoscanning technique based on the release of specific mercury species from coal matrix during its gradual heating. Total mercury concentration and mercury thermospecies in coal were determined using Zeeman mercury analyzer RA-915M coupled with PYRO-915+ attachment, which is a PC controlled atomizing system. Total mercury concentration in the studied coals of different ranks and metamorphism degree were found to be within a range of less than 2 ppb up to 7600 ppb. The thermoscanning reveals the presence of various mercury thermospecies in coal, which could be subdivided in the low-temperature species, which are released at a temperature below 200 °C. They can be attributed to elemental mercury bound to coal matrix by physical sorption and occlusion. The appearance of the mid- and high- temperature species could be attributed to mercury bound to organic coal matrix, sulfides (mainly pyrite, FeS<sub>2</sub>), and clay minerals. The scanning electronic microscopy and electron probe microanalysis reveal the points of mercury accumulation, up to tenths percent by weight, in organic matrix and inorganic impurities.

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## Features of LIBS under the action of ultrasound.

Alexey Bulanov<sup>\*A,C</sup>, Ivan Nagorny<sup>B,C</sup>

<sup>A</sup> I.I.Ichev Pacific Oceanological Institute, 43, Baltiyskaya Street, Vladivostok, 690041, Russia;

<sup>B</sup> Institute for automation and control processes, 5, Radio Street, Vladivostok, 690041, Russia;

<sup>C</sup> Far Eastern Federal University, 8 Suhanova St., Vladivostok, 690950, Russia.

\*a\_bulanov@me.com

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**ABSTRACT:** The method of laser induced breakdown spectroscopy (LIBS) was used to investigate intensive lines of sodium, calcium in the dissolved solutions under the action of ultrasound at the frequencies of 10.7 kHz and 60 kHz. To excite optical breakdown in water we used a Nd:YAG laser with the wavelength of 532 nm, a pulse duration of 10 ns and pulse energies of up to 180 mJ (in a modulated Q-mode). Acoustic radiation was generated within of cylinder transducers using a digital generator and powerful amplifier with maximum amplitude of 100 kPa. To excite optical breakdown in water we used a Brilliant B Nd:YAG laser with an emission wave length of 532 nm, a pulse duration of 10 ns, and pulse energies of up to 500 mJ (in a modulated Q-mode). Acoustic radiation was generated using a digital generator of arbitrarily shaped signals and broad band amplifier with maximum amplitude at a resonance of 100 kPa. The problem of synchronization of acoustic and optical radiation was solved. Generator of delays was used for the best results of interaction of acoustic and optical radiation. Thus, the effect of magnification of Na and Ca spectral lines intensity for salt water under the influence of an ultrasound field was found. It should be noted that the intensity of the ion Ca line depends on the phase of ultrasound field as well. The obtained results indicate the possibility of increasing the efficiency of laser-induced breakdown spectroscopy of a liquid in the ultrasound field and allow you to talk about the possibility of application of ultrasound in technology LIBS. This work was supported by the Russian Foundation for Basic Research (project 16-02-00841-a).

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## Evaluation of compact VUV spectrometer for elemental imaging by laser-induced breakdown spectroscopy

S. Moncayo<sup>\*A</sup>, F. Trichard<sup>A</sup>, D. Devismes<sup>B</sup>, F. Pelascini<sup>B</sup>, A. Feugier<sup>C</sup>,  
C. Sasseville<sup>D</sup>, F. Surma<sup>E</sup>, V. Motto-Ros<sup>A</sup>

<sup>A</sup>Institut Lumière Matière UMR 5306, Université Lyon 1 - CNRS, Université de Lyon 69622  
Villeurbanne, France; <sup>B</sup>CRITT Matériaux Alsace, 67305 Schiltigheim, France; <sup>C</sup>Ocean  
Optics Incorporate, Dunedin, Florida 34698, United States; <sup>E</sup>Géocoop, 5573 Hippolyte-  
Lancôt street, Montreal (Quebec) Canada H1K 5G6; <sup>F</sup>Epitopos, 4 Boussingault Street,  
Strasbourg 67000 France.

\*samuel.moncayo@univ-lyon1.fr

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**ABSTRACT:** This work presents a novel approach to perform LIBS elemental imaging in the vacuum ultraviolet (VUV) wavelength range by using an Argon purge probe couple to a compact spectrometer. In spite of several important elements for geological and mineralogical science such as, P, S, As, B, C, or Zn presenting strong lines in the VUV range, the need of using specific optics and working under free-oxygen conditions has limited the extension of LIBS systems able to work in this range. Herein, we present an adaptation of our LIBS imaging experimental design to access to the VUV working at atmospheric pressure. The system is based on an optical probe directly couple to a MayaPro compact spectrometer (Ocean Optics, covered range 150-250 nm), the all being purged with argon. In this work, the technical design along with a detailed evaluation of the VUV probe is addressed. The possibility to use this VUV probe for LIBS imaging is also investigated by studying a Canadian mining core sample with special emphasis to the detection of sulfur. In addition to Sulfur, more than 15 elements including P, As, C, Ca, Si, Mo, B, and Zn have also been detected. Elemental images covering sample surfaces in the range of cm<sup>2</sup> with a micrometric spatial resolution (< 10 μm) are presented. A limit of detection of 0.22 wt% for Sulfur is demonstrated in a single shot configuration. Along with silicates, borosilicates and carbonates phases, three sulfur mineral phases, i.e. chalcopyrite (CuFeS<sub>2</sub>), pyrite (FeS<sub>2</sub>) and molybdenite (MoS<sub>2</sub>) have also been clearly identified. These results show the feasibility of LIBS imaging to work in the VUV range evaluating from the technical and practical point of view the potential use of laser spectroscopy in geology and mine applications.

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## Development of different quantification strategies for in-depth profile analysis of NiCu/Cu layers and multilayers via pulsed glow discharge time-of-flight mass spectrometry

Rocío Muñiz<sup>\*A</sup>, Lara Lobo <sup>A</sup>, Katalin Németh <sup>B</sup>, László Péter <sup>B</sup>, Rosario Pereiro<sup>A</sup>

<sup>A</sup>Department of Physical and Analytical Chemistry, Faculty of Chemistry, University of Oviedo, Julián Clavería 8, 33006, Oviedo, Spain. <sup>B</sup> Wigner Research Centre for Physics, Hungarian Academy of Sciences, Konkoly-Theget út 29-33, H-1121 Budapest, Hungary.

\*rociomunizdelgado@gmail.com

**ABSTRACT:** Electrodeposited multilayers and compositionally modulated alloys are innovative materials of interest due to their mechanical, magnetic and corrosion properties and so they need to be characterized in terms of layer structure and composition. Pulsed glow discharges (PGD) coupled to time-of-flight mass spectrometry detection (TOFMS) offers great potential for in-depth profile analysis of these types of materials as it allows high acquisition rates and good mass resolution together with depth resolution in the nanometer range. Moreover, due to the low intrinsic matrix effects of this technique, it allows not only for qualitative (signals versus sputtering time) information but also for quantitative results (concentration versus sample depth). Nevertheless, there is still a lack of analytical quantitative approaches to achieve this last aim, especially when dealing with PGD sources. The purpose of this work is to develop and evaluate different quantification procedures for PGD-TOFMS. In particular, research was focused towards the characterization of samples consisting on NiCu/Cu layers and multilayers electrodeposited on Si wafers with total thicknesses ranging between 200 nm and 800 nm and individual NiCu & Cu layers of at about 80 nm.

PGDs are characterized by three different regions due to the temporal application of the applied power: prepeak (just at the beginning of the applied power), plateau (during the duration of the power) and afterglow (after the applied power is off). This last region is the most sensitive one and so it is very convenient for quantitative analysis of the minor components, however, major components are often saturated. For such cases, we have investigated two different strategies based on a multi-matrix calibration procedure: (i) using the afterglow region for all the sample components except for the major element (Cu) that was analyzed in the plateau, and (ii) using the afterglow region for all the components but instead of Cu measuring the ArCu signal. Quantitative depth profiles obtained with these two strategies were in well agreement with the expected values from the electrodeposition process, both in terms of thickness and composition of the layers.

## Investigation of the layer-thickness- and wavelength-dependence of laser stratigraphy on Cu and Ni coatings using LIBS

Tristan O. Nagy\*<sup>A</sup>, Evgeniya Paulis<sup>A</sup>, Morris J.J. Weimerskirch<sup>B</sup>, Ulrich Pacher<sup>A</sup>, Wolfgang Kautek<sup>A</sup>

<sup>A</sup>Department of Physical Chemistry, University of Vienna, Währingerstrasse 42, 1090 Wien, Austria;

<sup>B</sup>Faculty of Physics, University of Vienna, Boltzmannngasse 5, 1090 Wien, Austria.

\*tristan.nagy@univie.ac.at

**ABSTRACT:** The rapid qualitative and quantitative stratigraphic 3D-analysis of metal coatings, in particular on structured samples, is of substantial importance in modern industrial and medical QC/QA routine. Laser-Induced Breakdown Spectroscopy (LIBS) is one of the most promising options to receive fast and reliable results in this field<sup>1</sup>. Consequently, finding the optimal parameters for the analysis of given systems is a crucial task. Furthermore the knowledge of the ablation properties in combination of laser-induced heat transfer allow for the development of custom analysis and machining approaches for composite layered materials.

In this Study, various galvanic coatings of Cu and Ni at different thicknesses (5, 10, 15 and 20  $\mu\text{m}$ ) typically applied in industrial standard routines were investigated. Ablation experiments were carried out using the first two harmonic wavelengths of a pulsed Nd:YAG laser (1064 and 532 nm), and the resulting plasma spectra were analysed using the correlation method<sup>2,3</sup>. For both wavelengths, the ablation behaviour, effective absorption coefficient and LIBS depth profiles were studied in relation to the layer thickness and compared to corresponding theoretical values<sup>4</sup> originating from common thermal ablation models.

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## Proposition of Classification Models by Near-Infrared Spectroscopy for Quality Evaluation of Cattle Leathers

Carlos Eduardo M. Braz<sup>\*A,B</sup>, Ana Rita A. Nogueira<sup>A</sup>, Manuel Antonio C. Jacinto<sup>A</sup>, Gilberto B. Souza<sup>A</sup>

<sup>A</sup>Embrapa Pecuária Sudeste, São Carlos, SP, 13560-970, Brazil; <sup>B</sup>Grupo de Análise Instrumental Aplicada, Departamento de Química, Universidade Federal de São Carlos, São Carlos, SP, 13565-905, Brazil.

\*carloredumb@yahoo.com.br

**ABSTRACT:** In order to determine the quality of the leathers after tanning process, we construct models by near-infrared spectroscopy (NIRS) based on physical and mechanical tests, which allowed us to assess the capacity of the leathers to withhold the wear and tear of automotive upholstery, shoes, clothing, furniture, and other accessories. The following official methods were used: tensile strength, percentage elongation, tear strength, and tear strength double hole. To obtain reference values for the classification models, we used 314 samples of cattle leather tanned with chromium, 201 of finished leather and 113 of semi-finished ones. All samples were previously conditioned for 48 h at  $23 \pm 2$  °C and relative humidity of  $50 \pm 5\%$ . The standard procedure for testing the leather quality was divided in longitudinal (L) and transversal (T) directions. Samples from L and T directions were obtained parallel to the cranial-caudal axis of the animal, according to ABNT NBR ISO 2418:2015. With a hydraulic press, 3 samples in the L and 3 in the T directions of each sample were collected, and the thicknesses of the test specimens were measured. A dynamometer was used to carry out the determination of the evaluated physical and mechanical tests, and the average values between L and T were used as reference values. The near infrared spectrums were obtained in an NIRFlex N-550 Solids (BUCHI, Flawil, Switzerland) with resolution  $4\text{ cm}^{-1}$ , 32 scans and spectral region from 4000 to  $10000\text{ cm}^{-1}$ . To construct the classification models we applied the K-nearest neighbor (KNN), the soft independent modeling of class analogy (SIMCA), and the partial least squares – discriminant analysis (PLS-DA). Two classes were considered to evaluate the models: tensile strength class 1: 10.00-24.08 and class 2: 24.13-43.75  $\text{N mm}^{-2}$ ; percentage elongation class 1: 46.41-77.90 and Class 2: 78.10-116.92 %; tear strength class 1: 62.41-108.19 and class 2: 108.20-262.39  $\text{N mm}^{-1}$ ; and strength tear double hole class 1: 62.67-99.83 and class 2: 100.17-274.17 N. The calculated calibration and validation models have satisfactory results, with prediction percentages ranging from 87% to 100%. Otherwise, tensile strength ranged from 52 to 81%. We divided the dataset into calibration and validation and calculated their accuracy, sensitivity, and specificity. All figures of merits for tensile strength were relatively low, from 52% to 66% (KNN), from 61% to 74% (SIMCA) and from 64% to 71% (PLS-DA). Otherwise, for percentage elongation, tear strength and strength double holes the lowest percentage of validation model was 92% (KNN), and the highest one was 100% (PLS-DA). The models generate concordant predicted results with the reference values. The abilities of the models were similar, showing that it can be used to predict the cattle leather quality. However, to improve the tensile strength hit rate model, the inclusion of more variable samples is required.

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## Te UV-photochemical vapour generation

Eliska Novakova<sup>\*A</sup>, Zuzana Melichova<sup>B</sup>, Jakub Hranicek<sup>A</sup>

<sup>A</sup>Faculty of Science, Charles University, Albertov 6, Prague 2, Czech Republic;

<sup>B</sup>Faculty of Science, Matej Bel University, Tajovského 40, Banská Bystrica, Slovak Republic

\*eliska.novakova@natur.cuni.cz

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**ABSTRACT:** The technique of volatile species generation has recently seen renewed interest due to the development of new generation approaches. The main advantage of this technique is the separation of the analyte from the sample matrix and the subsequent possibility to decrease spectral interference and improve the limits of detection in comparison with the direct analysis of liquid samples using atomic spectrometric methods. Photochemical vapour generation offers the further advantage of pre-reduction of elements from the 16<sup>th</sup> group of the periodic table. Te was selected as model for less stable volatile compounds from the above mentioned group.

Te volatile species were generated from sodium tellurite and telluric acid using TiO<sub>2</sub> assisted UV-photochemical generation and they were detected in quartz furnace by AAS. It was found that generation of volatile compound is possible from formic and acetic acid using a 20W germicidal lamp. The results are compared to TiO<sub>2</sub> assisted UV-photochemical generation of Se (IV) and Se (VI). Sources of different behaviour of Te (IV) and Te (VI) with regard to reaction time are described and discussed. The volatile compound was indeed found less stable than Se species generated at similar conditions and prone to decomposition at laboratory temperature. Decrease of temperature at the outflow from the UV-photochemical reactor was sufficient for the deposition of fine coating of reduced Te on the transport tubing. The problems with reduced stability of Te volatile compound should be addressed. Volatile compound derived from Te (IV) was also generated without the use of photocatalyst and the attained results are discussed too.

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## Various aspects of sulfur determination in concrete samples using Laser Induced Breakdown Spectroscopy

Aleš Hrdlička<sup>\*A</sup>, Jitka Hegrová<sup>B</sup>, Karel Novotný<sup>C,D</sup>, Viktor Kanický<sup>A,C</sup>, Pavel Pořízka<sup>D,E</sup>, Lucia Sládková<sup>E</sup>, David Procházka<sup>D,E</sup>, Jan Novotný<sup>D,E</sup>, Jakub Klus<sup>D,E</sup>, Pavlína Škarková<sup>E</sup>, Jozef Kaiser<sup>D,E</sup>

<sup>A</sup>Masaryk University, Central European Institute of Technology, Kamenice 753/5, Brno, 62500, Czech Republic; <sup>B</sup>Transport Research Centre, Líšeňská 33a, Brno, 63600, Czech Republic; <sup>C</sup>Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, Brno, 61137, Czech Republic; <sup>D</sup>AtomTrace a.s., Vědecko-technický park profesora Lista, Koleční 9, Brno, 61200, Czech Republic; <sup>E</sup>Brno University of Technology, Central European Institute of Technology, Purkyňova 123, Brno, 61200, Czech Republic.

\*ahrdlicka@chemi.muni.cz

**ABSTRACT:** Analysis of concrete is one of the auspiciously developing industrial applications of Laser Induced Breakdown Spectroscopy (LIBS). Knowing the content of chlorine, fluorine and sulfur can be decisive on the current state and security of a particular concrete construction. The sulfur amount in the used cement as a binder of gravel stones in a concrete can influence its solidness. Determination of sulfur in several samples of concrete samples from traffic constructions is the subject of this work. Such task, however, requires more than basic LIBS equipment. Similar to other non-metals, sulfur excitation energies are high and most sensitive emission lines fall to the vacuum ultraviolet range and several much less sensitive lines can be found in visible and lines with higher intensity in near-infrared (NIR) region. To ever visualize the sulfur NIR lines it is often necessary to remove oxygen from the sample neighborhood and to enhance them, helium atmosphere is necessary as well as its pressure should be lowered and further optimized. Owing to the stronger plasma expansion and faster decay of hard lines also the gate delay should be optimized and shifted down to several hundreds of ns. These measurement conditions and parameters and moreover some interference on the emission line S I 921.28 nm were investigated and optimized. The best conditions for maximum lines intensities may not be sometimes applicable due to a parallel increase of an adjacent interfering line. The used LIBS equipment is a SciTrace (AtomTrace) instrument consisting of a 532 nm Q-switched Nd:YAG laser vertically ablating a sample and producing craters of about 0.23 mm in diameter at the pulse energy of 100 mJ. The improvement in detected intensity was investigated in helium atmosphere under various underpressures in a sealed LIBS interaction chamber (AtomTrace). The average content of sulphur was about 0.1-0.3 wt. % by a reference standard procedure employing gravimetry and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). As the LIBS analysis is a spatially resolved method, several spots on the stones without measurable sulfur content were found while the others, in the cement binder, indicate sulfur presence. The obtained sulfur amount from the particular ablation spots is not directly comparable with ICP-MS but a representative average must be taken into account. Simple method using a synthetic limestone enriched by defined amounts of Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O was used for achieving the calibration dependence for studied element. This powder material was pressed into pellets and different matrix responses were corrected using selected spectral lines as internal standards.

## Experimental Results from Purification of TlBr Semiconductor Crystals by the Filter Method for Use as Gamma-ray Detectors

Toshiyuki Onodera<sup>\*A</sup>, Keitaro Hitomi<sup>B</sup>, Tadayoshi Shoji<sup>A</sup>

<sup>A</sup>Faculty of Engineering, Tohoku Institute of Technology, Sendai, Japan; <sup>B</sup>Cyclotron and Radioisotope Center, Tohoku University, Sendai, Japan.

\*t\_onodera@tohotech.ac.jp

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*ABSTRACT: Thallium bromide (TlBr) compound semiconductor crystal is known as a state-of-the-art high energy gamma-ray detector material due to their high atomic numbers (Tl: 81 and Br: 35), high density ( $7.56 \text{ g/cm}^3$ ) and high charge transport properties (electrons:  $\sim 10^{-3} \text{ cm/V}$  and holes:  $\sim 10^{-4} \text{ cm/V}$ ). The filter method has been studied as one of the promising purification methods, which can obtain TlBr with moderate purity from a low purity TlBr material more readily and rapidly. In this study, ceramic instruments were used to trap impurities in a starting TlBr powder and TlBr crystals were grown from the purified material. Gamma-ray spectral responses and electronic characteristics such as current-voltage curves and charge transport properties were evaluated using TlBr detectors fabricated from the grown crystals.*

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## Removal of metals and dyes in wastewater treatment by surface modified PP resins

Francesca Cicogna<sup>\*A</sup>, Massimo Onor<sup>A</sup>, Stefano Javarone<sup>A</sup>, Elisa Passaglia<sup>A</sup>, Serena Coiai<sup>A</sup>

<sup>A</sup>Istituto di Chimica dei Composti Organometallici ICCOM CNR PISA, Via G. Moruzzi 1 Pisa, Italy.

\*francesca.cicogna@pi.iccom.cnr.it

**ABSTRACT:** The surface modification of polypropylene spheres (PPs) with different functional groups was carried out by photografting polymerization. By this method, polar functional groups were immobilized onto PPs surface with the aim to change the surface polarity and possibly the affinity with other polar substances. Different vinyl monomers bearing polar groups were chosen on the basis of their possible interactions with potentially dangerous metals and dyes that can be present in wastewaters. The modified resins were characterized by ATR-FTIR analysis to confirm the presence of functional groups onto PPs surface, whereas the amount of immobilized functionalities was determined gravimetrically. The so obtained resins were then used in the wastewater treatment for the removal of metals. In particular, tests were carried out by suspending the resins in aqueous solution of copper, cadmium, lead, zinc and mercury at two pHs (2 and 5.5). The obtained resins were also tested in the removal of other potentially dangerous species like dyes and iodine. Indeed, in agreement with the known ability of poly(acrylic acid) to retain some dyes, resins modified with acrylic acid (AA) and with 2-acrylamido-2-methylpropane sulfonic acid (AMPS) were tested in the removal of crystal violet (CV) from water. CV is a triarylmethane dye used as a histological stain and in Gram's method of classifying bacteria, but it was also reported to be dangerous to human health. Whereas resins modified with N-vinylpyrrolidone (NVP) were used to remove iodine from water solutions. Also in this case, the reactivity of poly(NVP) with iodine that gives the "iodopovidone" (an antiseptic used for skin disinfection) was exploited to remove iodine from water solutions. In particular, resins bearing different functional groups were suspended in water solutions containing different metal ions, dye or iodine. The amount of the metals in solutions before and after the contact with the modified resins was determined by using an Inductively Coupled Plasma Mass Spectrometry (ICP-MS) that is a mass spectrometer generally used for elemental determinations and can detect metals and several non-metals at concentrations as low as one part in  $10^9$  ( $\mu\text{g/Kg}$ ). The ions of the elements formed by ionization with ICP were separated and quantified by a coupled mass spectrometer. UV-Vis spectroscopy was instead used to evaluate the amount of CV or iodine removed by PP-AA, PP-AMPS or PP-NVP. The data so far obtained evidenced that the ability to retain metals depends on the type of functional groups bonded onto the PPs surface and on the pH of the metal solutions. Interestingly, an almost quantitative removal of mercury was observed by using PPs resin functionalized with 2-(dimethylamino)ethyl methacrylate (DMA) at pH 2. Whereas about 80% of copper and cadmium were retained by PPs modified with AA. The modification of the resins and their characterization as well as the retention of metals and dye will be discussed.

## Development and application of ICP-MS methodologies for trace elements, As species and Pb isotope ratios determination in Mediterranean sponges

Anna Maria Orani <sup>\*A,B</sup>, Emilia Vassileva <sup>B</sup>, Olivier Thomas <sup>B,C</sup>, Aurélie Barats <sup>A</sup>

<sup>A</sup>Université de Nice Sophia Antipolis, CNRS, IRD, Observatoire de la Côte d'Azur, Géoazur UMR 7329, 250 rue Albert Einstein, Sophia Antipolis 06560 Valbonne, France (aurelie.barats@unice.fr); <sup>B</sup>International Atomic

Energy Agency, Environment Laboratories, 4 Quai Antoine 1er, Monaco (e.vassileva-veleva@iaea.org);

<sup>C</sup>National University of Ireland Galway, Marine Biodiscovery, School of Chemistry, University Road, Galway, Ireland (olivier.thomas@nuigalway.ie)

\*anna-maria.orani@geoazur.unice.fr

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**ABSTRACT:** Coastal marine ecosystems in many parts of the world are under unrelenting stress caused by urban development, pollutants and other ecological impacts. Trace elements (TE) originating from both natural and contaminated sources, enter marine ecosystems through different sources. The need of monitor the TE levels and their environmental impact is constantly increasing. Considering that seawater analysis presents relevant analytical problems (due to the saline matrix, interferences and low TE contents) and that sediments are not always available, especially in rocky shores, recent studies have been focused on TE measurements in living organisms. Sponges are convenient bio-monitors since they are sessile filters feeders, available in many coastal areas and they have already shown a great ability of TE accumulation. In this work, four different Mediterranean sponge species were studied and their intra and inter-specie variation were evaluated with regards to trace elements accumulation and bio-transformation. Four species were selected because of their wide distribution in the western Mediterranean Sea but also for the differences in morphologic characteristics which could reflect differences in trace elements accumulation. At least three specimens of each specie were collected by scuba diving during two sampling campaigns, in February and September 2016, in order to evaluate possible seasonal variations. Trace elements (V, Mn, Co, Ni, Cu, Zn, As, Sr, Mo, Ag, Cd, Ba, Pb, U) were determined by ICP (Q) MS after acid digestions assisted by microwaves. Hg content was measured directly on solid samples by AMA (Advanced Mercury Analyzer). Pb isotope ratios, used as analytical tool for tracing global and local pollution sources, were measured by HR-ICP-MS. Since sponges have already shown the capability of transforming some elements during their metabolic processes, a methodology for Arsenic speciation by HPLC-ICP-MS was also developed. The development of speciation method included optimization of several analytical steps, as chemical extraction, HPLC elution gradient and mobile phase composition among others. Quality control procedures were assured by regular use of different Certified Reference Materials. Bioaccumulation Factors (BAF) calculated referring both, to concentration normally found in seawater and contents measured in sediment samples collected in the same area, changed drastically depending on the element and on sponge specie, reaching values in the range of 50k-5M. This study represents the first complete work on trace elements accumulation, As speciation and Pb isotope ratios in Mediterranean sponges. Results have shown that bioaccumulation processes can vary depending on morphological features as well as on type of studied metal. Our results highlight the great capabilities of sponges as biomonitors of TE pollution and could be successfully employed in a "sponge watch program" alternative to the more common "mussel watch program".

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## Discrimination of Polymers By Using Laser-induced Breakdown Spectroscopy and Chemometric Techniques

Belgin Genc Oztoprak<sup>\*A,C</sup>, Erhan Akman<sup>A,C</sup>, Arif Demir<sup>B,C</sup>

<sup>A</sup>Faculty of Aeronautics and Astronautics, Kocaeli University, Kocaeli, Turkey; <sup>B</sup>Department of Physics, Kocaeli University, Kocaeli, Turkey; <sup>C</sup>BEAM Ar-Ge Optics, Laser and Spectroscopy, KOU Technopark, Kocaeli, 41275, Turkey

\*belgingenc@kocaeli.edu.tr

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*ABSTRACT: Laser-induced breakdown spectroscopy (LIBS) is a promising method for rapid identification and discrimination of materials by using advanced computerized chemometric techniques. All spectra of polymers have C, H, N and O atomic lines, CN and C2 molecular bands in atmospheric environment. The metallic elements such as Al, Ca, Mg, Na, K and Ti are used in polymers to reduce production cost or improve physical and mechanical properties. Spectral similarity of the composition of the material that share same elemental composition is the major problem of classification by LIBS. Therefore, LIBS spectra combined with multivariate data analysis methods to classify the samples. Discrimination of polymers is an important for recycling of plastics waste to prevent serious environmental challenges. In this study, classification of the polymers ( PET, PMMA, PP, PS, PVC) were performed by using LIBS and chemometric techniques such as PCA and PLS-DA for recycling purposes.*

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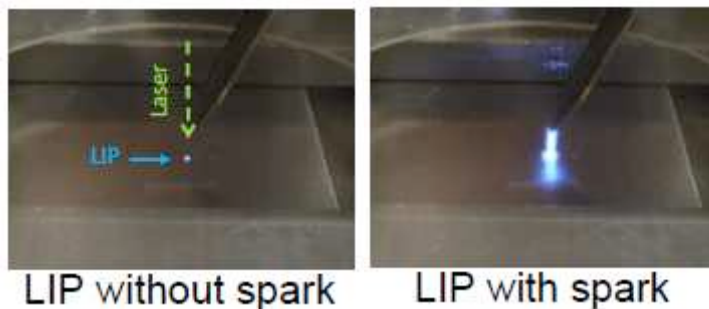
## Element imaging of metallic and dielectric layers by laser ablation - electric spark optical emission spectroscopy

Norbert Huber<sup>\*A</sup>, Sandra Donninger<sup>A</sup>, Josef Hofstadler<sup>B</sup>, Andreas Pissenberger<sup>B</sup>, Hubert Duchaczek<sup>B</sup>, Johannes D. Pedarnig<sup>\*A</sup>

<sup>A</sup> Institute of Applied Physics, Johannes Kepler University, Altenberger Straße 69, 4040 Linz, Austria; <sup>B</sup> voestalpine Stahl GmbH, A-4031 Linz, Austria

\*johannes.pedarnig@jku.at

**ABSTRACT:** Element images of metallic and dielectric layers on metal substrates are recorded by a raster-scanning optical emission spectroscopy (OES) and hyperspectral imaging. Plasma is induced on the sample surface by Nd:YAG (532 nm, 1064 nm) laser ablation and is cross-excited by electric spark discharge ( $U = -2.5$  kV). Emission spectra are recorded using a compact grating spectrometer with CCD line detector. We investigate the dependence of emission line intensities on the laser energy ( $E$ ) and spot diameter ( $d$ ) and on the parameters of the electric discharge circuit. Furthermore, we apply this OES method to the 2D element imaging of patterned samples like Cu thin films on Al, photoresist layers on Si, and human fingerprints and electrically insulating inorganic layers on Al. The electric spark is guided to the laser-induced plasma (LIP) and without laser ablation the spark is suppressed (Figure). The laser pulse energy required to induce and cross-excite an analytical plasma is low ( $E \leq 1$  mJ,  $d \approx 100$   $\mu$ m). The optical emission of such plasma is intense and the plasma persistence time is several tens of microseconds depending on the electric circuitry. Without spark discharge the plasma emission is very faint and it vanishes within few microseconds. For the combined plasma the measured emission line intensity of major elements correlates with the thickness of the sample layer. The intensity of minor elements in the underlying metal substrates correlates with their concentration. The achievable spatial resolution of spectrochemical images depends on the size of the laser spot and of the sparked area ( $>60$   $\mu$ m). The chemical contrast of element images is higher with the cross-excited plasma ( $E \approx 1$  mJ) than with the laser-induced plasma at higher energy ( $E \approx 10$  mJ).



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## Assessment of Next Generation Thin Film Solar Cells by Depth Profile Analysis using Pulsed Glow Discharge – Time of Flight Mass Spectrometry

Beatriz Fernández<sup>A</sup>, Lara Lobo<sup>A</sup>, Pascal Sanchez<sup>B</sup>, Armando Menendez<sup>B</sup>, Nies Reininghaus<sup>C</sup>, Vasil Stoichkov<sup>D</sup>, Jeff Kettle<sup>D</sup>, Rosario Pereiro<sup>\*A</sup>

<sup>A</sup>Department of Physical and Analytical Chemistry, University Of Oviedo, C/Julian Clavería 8, Oviedo, Spain; <sup>B</sup>Energy Area (EN), ITMA Foundation, Avilés (Spain); <sup>C</sup>Next Energy, Carl-von-Ossietzky-Str. 15, 26129 Oldenburg (Germany); <sup>D</sup>Bangor University, School of Electronic Engineering, Dean Street, Bangor, Gwynedd, UK LL57 1UT (Wales, UK).

\*mrpereiro@uniovi.es

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**ABSTRACT:** Photovoltaic solar cell performance strongly depends on parameters such as layer thicknesses, dopant element concentrations, presence of impurities and diffusion processes. Reliable solid-state spectrometric techniques, such as pulsed glow discharge (PGD) sources coupled to mass spectrometry (MS), provide a powerful tool for depth profiling analysis of conducting and non-conducting materials with high depth resolution. In general, next generation thin film solar cells (TFSCs) have lower material usage, energy payback times and potentially lower production costs compared to traditional crystalline silicon solar cells. However, they possess drawbacks including lower efficiency and worse stability to light outdoor stress factors. PGD-MS was applied to the depth profile characterization of different type of thin film solar cells, including hydrogenated amorphous silicon (a-Si:H), tandem-junctions solar cells, and perovskite solar cells. Fast and sensitive qualitative and quantitative (a-Si:H solar cells) determination of matrix and dopant elements in different types of solar cells have been successfully performed by PGD-MS. Elemental diffusion processes between the coating layers were identified for a-Si:H and tandem-junctions solar cells. Concerning perovskite and tandem-junction solar cells, different synthesis processes were evaluated and variation in the distribution of dopant elements was found as a result of different sample preparation steps. Therefore, this depth profile procedure can be used as an analytical tool to provide feedback to manufacturers who can further develop the thin-film solar cell sample preparation.

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## Characterisation of commercial alizarin-based lakes by means of spectroscopic techniques.

Pronti Lucilla<sup>\*A</sup>, Jean-baptiste Mazzitelli<sup>B</sup>, Maria Paola Bracciale<sup>C</sup>, Lorenzo Massini Rosati<sup>A</sup>, Anna Candida Felici<sup>A</sup>, Cathy Vieillescazes<sup>B</sup>, Maria Laura Santarelli<sup>C</sup>

<sup>A</sup>Dipartimento di Scienze di Base e Applicate per L'ingegneria, Sapienza-University of Rome, via Antonio Scarpa 16-00161 Rome, Italy; <sup>B</sup>Restoration engineering of Natural and Cultural Heritage – IMBE UMR 7263 CNRS – IRD 237, University of Avignon, Campus Jean-Henri Fabre - 301 rue Baruch de Spinoza - BP 2123984916 Avignon Cedex, France; <sup>C</sup>Dipartimento di Ingegneria Chimica Materiali Ambiente and CISTeC-Centro di Ricerca in Scienza e Tecnica per la Conservazione del Patrimonio Storico Architettonico, Sapienza-University of Rome, in via Eudossiana 18-00184 Rome, Italy.

\*lucilla.pronti@uniroma1.it

**ABSTRACT:** The red dyes were commonly used as artists' materials since ancient times. They are organic substances based on the anthraquinonic structure and can be achieved from insects, such as cochineal (carminic acid), kermes (kermesic acid) or can be extracted from plants, such as madder (mainly composed by alizarin). To use them in paintings, the dyes were mixed with an insoluble substrate such as aluminium hydrated, calcium carbonate or calcium sulphate; the name "lake" is referred to this latter procedure.

In this work fifteen alizarin-based lakes, produced by Kremer-Pigmente and Zecchi, have been studied in order to investigate their optical and chemical features by means of Energy Dispersive X-ray Fluorescence (EDXRF), Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy (ATR-FTIR), X-ray Powder Diffraction (XRD), Liquid Chromatography coupled with a Photodiode Array (LC-PDA), UV fluorescence and reflectance spectroscopies.

Almost all the lakes show alizarin as main organic compounds, one of them (23610-Kremer) presents only this anthraquinonic, indicating a synthetic dye. Lucidin primeveroside and ruberythric acid are detected in some lakes suggesting the use of "Rubia tinctorum". Most of the samples contain typical compounds present in the natural roots of madder but in two lakes (23600-Kremer and alizarin crimson-Zecchi) any anthraquinonic compounds were detected, thus they are probably synthetic dyes, as 23610 (Kremer).

Furthermore several inorganic substrates, probably added during the manufacturing process, were detected.

From the results obtained by UV fluorescence spectroscopy it is possible to conclude that, although it is commonly assumed that the madder lake presents an orange-pink fluorescence, the inorganic compounds induce a quenching phenomenon or an inhibition of the fluorescence.

## Depth Profile Analysis of Thin Films Using Laser-Induced Breakdown Spectroscopy

Lukáš Průcha<sup>A\*</sup>, Pavel Pořízka<sup>A</sup>, David Prochazka<sup>A</sup>, Jakub Klus<sup>A</sup>, Jan Novotný<sup>A</sup>, Karel Novotný<sup>A</sup>, Jozef Kaiser<sup>A,B</sup>

<sup>A</sup>CEITEC BUT, Central European Institute of Technology Brno University of Technology, Technická 3058/10, 616 00 Brno, Czech Republic; <sup>B</sup>AtomTrace, a.s., Kolejní 3094/9, 612 00 Brno, Czech Republic

\*lukas.prucha@ceitec.vutbr.cz

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*ABSTRACT: For the past decade, the use of thin films (50 nm – 1,5 µm) in industry is on the rise. In many industrial sectors it is necessary to use thin films to improve the properties of materials and the development of new components dependent on precisely manufactured homogeneous thin films. Real time and in-situ quality control is therefore of key importance. As we have also proved, Laser-Induced Breakdown Spectroscopy (LIBS) technique enables to assess the elemental distribution in surface coating. In LIBS depth profile analysis, layers of material are ablated individually with high depth resolution (~100 nm) and thickness of the coating can be estimated. The main goal of this work was to achieve the best depth resolution possible on the Sci-Trace instrument. Those research efforts were undertaken in order to employ LIBS technology in the analysis of thin films, where the thickness is typically under one micron. The optimization process was focused namely on depth resolution and stability (repeatability and reproducibility). The optical profilometer was used in order to study the crater morphology.*

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## Investigation of mussel adhesive protein inspired coatings by X-Ray Photoelectron Spectroscopy: screening of optimal conditions for biomolecule conjugation.

Elisabetta Mazzotta\*, Simona Rella, Antonio Turco, Antonio Caroli, Cosimino Malitesta

Dipartimento di Scienze e Tecnologie Biologiche e Ambientali (Di.S.Te.B.A.), University of Salento,  
via Monteroni 73100 Lecce, Italy

\*elisabetta.mazzotta@unisalento.it

**ABSTRACT:** Among the available surface functionalization methods performed in the wet state, only very few allow for the formation of a functional and uniform coating on a large variety of substrates in a single step. Among these, the deposition of polydopamine films from a basic solution of dopamine has emerged as a simple and effective way to form multifunctional polymer coatings on virtually any substrates<sup>1</sup>. Inspired by the composition of adhesive proteins in mussels, dopamine self-polymerization has been used to form thin, surface-adherent polydopamine films onto a wide range of organic and inorganic materials, including noble metals, oxides, polymers, semiconductors and ceramics. Although polydopamine deposition mechanism as well as its chemical composition are not precisely known, catechol and quinone functional groups are believed to be present in the polydopamine coating, the latter of which are capable of covalent coupling to nucleophiles. The reactivity of polydopamine films towards amine and thiol groups has been ascribed to reactions between nucleophiles and polydopamine surface and has been exploited to covalently immobilize biomolecules onto its surfaces<sup>2,3</sup>.

In the present study, polydopamine films have been deposited on gold surfaces from stirred basic solutions (pH 8.5) by auto-oxidation of dopamine at different time intervals (namely, 1, 3, 5, 8, 18, and 24 hours). On the basis of the reported effect of oxygen in increasing the reaction kinetics of alkaline dopamine oxidation<sup>4</sup>, polydopamine deposition has been performed in the same conditions under a pure oxygen environment. Moreover, for a comparison, polydopamine coatings have been prepared also by exploiting chemical dopamine oxidation in the presence of a strong oxidizing agent for the same time intervals and electrochemical oxidation by cyclic voltammetry. As prepared samples have been investigated by X-Ray Photoelectron Spectroscopy (XPS) with the aim to identify chemical functionalities and to estimate film thickness as a function of deposition time, under each tested conditions. Comparison of XPS data about elemental composition, distribution of functional groups and thickness of polydopamine coatings provided valuable information for identifying more suitable polydopamine coatings for biomolecules anchoring, thus further advancing the use of polydopamine as a modification layer for several applications.

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## Development of XPS in application to atmospheric particulate matter (PM) by comparison with results of Ion Chromatography

Simona Rella, Alessandra Genga, Cosimino Malitesta\*, Maria Siciliano

Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, University of Salento, Via Monteroni, Lecce, Italy

\*cosimino.malitesta@unisalento.it

**ABSTRACT:** Surface chemistry of atmospheric particulate matter (PM) has an important role in its environmental impact as it influences its toxicity at a large extent and some fundamental environmental process as radiation reflectivity, polar ozone depletion [1], etc.. XPS is a powerful technique in chemical characterization of solid surfaces as it produces elemental and speciation information, it does not generally require sample pretreatment and very low or no sample damage is observed. The high XPS LODs are somewhat compensated by the ability to detect trace chemical species concentrated at PM surface. XPS has been applied to atmospheric particulate matter (PM) soon after its invention [2] and interesting pieces of information have been obtained (see e.g. quite recently refs 3 and 4). Even so, its application is not mature, probably because accurate studies of correlation with results obtained by other more conventional spectroscopic and chromatographic techniques are necessary.

In this work, XPS results produced on PM collected in urban atmospheres and those of ion chromatography on water soluble fraction from the same samples are compared. Interesting correlations between results of the two techniques are evidenced.

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## Towards calibration transfer for quantitative analysis of nuclear materials by LIBS in the VUV range.

Edouard Rollin<sup>\*A</sup>, Jessica Picard<sup>A,B</sup>, Danièle Cardona<sup>B</sup>, Olivier Musset<sup>C</sup>, Jean-Baptiste Sirven<sup>A</sup>

<sup>A</sup>Den – Service d'Etudes Analytiques et de Réactivité des Surfaces (SEARS), CEA, Université Paris-Saclay, F-91191 Gif sur Yvette, France; <sup>B</sup>CEA, DAM, Valduc, 21120, Is-sur-Tille, France; <sup>C</sup>Université de Bourgogne Franche-Comté, Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR CNRS 6303, F-21078 Dijon, France.

\*edouard.rollin@cea.fr

**ABSTRACT:** To ensure the quality of their products, manufacturers of nuclear materials currently rely on wet chemistry methods coupled with ICP-MS and ICP-AES. These methods are slow and sometimes hard to implement, which leads the manufacturers to seek new possibilities of online, fast and direct preliminary quality control. Thus, the issue of quantifying metal impurities in both uranium and plutonium matrices by LIBS has been raised. As this problem is rarely addressed in LIBS, an innovative approach has been carried out, based on two main aspects. First, Vacuum Ultra-Violet (VUV) has been chosen as the spectral region of interest, which corresponds to wavelengths between 90 and 200nm. This choice is based on previous works in Glow Discharge Optical Emission Spectrometry<sup>1</sup> which may also be suitable in LIBS and showed that uranium and plutonium display fewer emission lines in the VUV and less background signal than in the UV-visible range, which is more favorable from an analytical point of view. Secondly, the lack of calibrated samples and the harsh security constraints hinder any possibility of complete analytical development on these materials. Therefore, the proposed method relies on calibration transfers from several non-nuclear metal matrices to uranium and plutonium matrices. Calibration transfers are widely studied and used in various spectrometry methods in order to overcome slope differences that appear in calibration lines between different measuring tools<sup>2</sup>, different elements or matrices. Here, the latter case will be studied: for each analyte, by measuring experimental data such as ablated mass and electron temperature (Te) and electronic density (Ne) of the plasma, normalizations of the LIBS signal of one line will be advanced to try to correct the slopes of the calibration curves and, ideally, end up with only one normalized calibration curve for all matrices. This uniformed calibration will then be used to quantify impurities in uranium and plutonium without having to make a full calibration on those matrices. Moreover, the above-mentioned experimental data will be empirically connected to the physical properties of the matrices, such as thermal diffusivity, boiling point etc... so that Te and Ne may be predicted in the nuclear matrices, where they may be harder to measure experimentally. Such an empirical model concerning the ablated mass has already been set up in a previous work<sup>3</sup>. This innovative approach aims to make the calibration transfer applicable for a wide range of metallic matrices while requiring minimal experimental measurements. Eventually, this work aspires for a better understanding of matrix effects, a major scientific issue in LIBS. This poster will describe the methodology that has been established and present the results of the earlier stages of this study.

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## **The road map towards providing a robust Raman spectroscopy-based cancer diagnostic platform and integration into clinic. Simultaneous Determination of Ten Elements in Doped $\text{Sr}(\text{NO}_3)_2$ Crystals by ICP-AES**

Shi Hongjun\*, Wang Li

Institute of Physics, Chinese Academy of Sciences, Beijing 100190, P.R.China

\*shihj@iphy.ac.cn

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*ABSTRACT: In this paper, an analysis method for simultaneous determination of ten elements Ag, Ca, Ce, Cu, Fe, La, Mg, Mn, Na and Zn in doped  $\text{Sr}(\text{NO}_3)_2$  crystals using ICP-AES was reported. The method of matrix matching and background correction was used to correct the matrix interference and spectral interference. The detection limits of the measured elements are 0.1-16  $\mu\text{g/L}$ , the recovery of synthetic samples are 90%–116%, and the relative standard deviation was less than 13%. This method is simple, rapid and accurate, and has been applied successfully to the analysis of sample with satisfactory results.*

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## Elemental analysis of glass samples and simulated vitrified nuclear wastes by LIBS

Fabio Spaziani\*, Tomohiko Kawakami, Yukio Hanamoto, Katsuyoshi Tatenuma

Kaken Co.Ltd., Hori 1044 - 310-0903 - Mito (Ibaraki), Japan

\*s.fabio@kakenlabo.co.jp

**ABSTRACT:** The analysis of glass samples is essential in various industries, since the elemental composition affects several physical properties (such as heat resistance or transparency) and consequently the quality. LIBS is an excellent technique for glass characterization, thanks to the capability of performing fast analysis without any sample preparation. Moreover, the glass matrix is also the basis of the vitrification process, that is the main technology for the stabilization and long-term storage of radioactive wastes. From this point of view, the possibility to operate in remote (such as with fiber-optic probe), joined to its essential immunity to the effects of ionizing radiation, makes LIBS a perfect choice for the monitoring activities in the nuclear area (not only the above-mentioned vitrified wastes but also monitoring inside plants under decommissioning).

In this study, we report the analysis of glass samples for the evaluation of LIBS performances on such type of materials. The analyses were planned and performed taking in account both the non-nuclear and nuclear applications. In fact, five types of glass samples whose composition included also nuclear-related elements (or elements with similar behavior) were produced in our laboratory and analyzed. The samples, therefore, had the characteristics of "simulated vitrified nuclear wastes", since cerium was used as a non-radioactive surrogate for uranium and plutonium. Our RI (Radioactive Isotope) research unit supervised the production of the samples, in order to develop a glass matrix as much similar as possible to real vitrified nuclear wastes. The samples included various amounts of Mo, Sr, Ce (as representative of elements related to nuclear wastes) inside a glass matrix (mainly made by Si and with Na, Ca, Mg, Al, Li and B). The amounts of the various elements were arranged in order to obtain an increasing trend similar to a calibration curve. This was important in order to check the LIBS performances on a wide range of concentrations and the linearity of the data measured.

The glass samples composition, and the confirmation of their successful production according to the defined concentrations, was determined by XRF analysis. Then, LIBS measurements were executed, by means of a commercial instrument (Applied Photonics LIBSCAN100) and using the silicon signal as internal standard to correct the instrumental drift.

Moreover, as additional validation of the LIBS results, glass-matrix matching certified reference materials (NIST 610-612-614) were analyzed.

The results showed excellent performances of the LIBS technique on the glass matrix, with a very good signal-concentration correlation ( $R^2 > 0.9$ ) for all the studied elements, even for the ones in low concentrations related to the monitoring activities in the nuclear industry. Therefore, the LIBS measurements showed a good agreement with those by XRF. Furthermore, the analysis of the NIST samples confirmed the reliability of the results and the good quality of the glass samples we made.

The availability of matrix matching materials with known concentration is the main factor in order to perform quantitative analysis, but the lack of solid calibration standards is still the main limitation of LIBS. However, thanks to the results obtained, our samples can be used as calibration material/reference material for fast quantitative LIBS analysis of glass materials.

Composition (as oxides, wt%) of the five simulated vitrified nuclear wastes					
Element	S-1	S-2	S-3	S-4	S-5
SiO <sub>2</sub>	38.425	53.446	65.878	69.191	73.115
Na <sub>2</sub> O	10	12.5	15	17.5	20
CaO	15	12.5	10	7.5	3.5
MgO	5	4	3	2	1
Al <sub>2</sub> O <sub>3</sub>	10	3.5	2	1	0.5
Li <sub>2</sub> O	10	5	0	0	0
B <sub>2</sub> O <sub>3</sub>	10	7.5	2	0.5	0
SrO	0.3	0.4	0.5	0.2	0.25
MoO <sub>3</sub>	0.4	0.024	0.012	1.3	0.8
CeO <sub>2</sub>	0.45	0.3	0.25	0.5	0.475

## **Ag<sup>+</sup> Coordination Polymers of a Chiral Thiol Ligand Bearing an AIE Fluorophore**

Dan-Dan Tao, Qian Wang, Xiao-Sheng Yan, Na Chen, Zhao Li and Yun-Bao Jiang\*

<sup>A</sup>Department of Chemistry, College of Chemistry and Chemical Engineering, the MOE Key Laboratory of Spectrochemical Analysis and Instrumentation, and the Collaborative Innovation Centre of Chemistry for Energy Materials (iChEM), Xiamen University, Xiamen 361005, China

\*ybjiang@xmu.edu.cn

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**ABSTRACT:** Coordination polymers facilitated by argentophilic interactions possess unique structure features and cause amusing photo-chemical and physical properties, widely applied as well. Here, we report that in the Ag<sup>+</sup> coordination polymers of a chiral thiol ligand containing an AIE fluorophore, tetraphenylethene (TPE), the TPE chromophores experience an H-type aggregation, yet a substantial enhancement of the fluorescence was observed, despite to a less extent than that in the aggregates of the thiol ligand itself which are of J-type. We show that this is not due to the difference in the freedom of the rotation of fluorophores in the two types of aggregates, but to a less extent of increase in the radiation rate constant in the coordination polymers while the much higher radiationless rate constant remaining more or less unchanged. Our findings here would be of significance for a comprehensive mechanistic understanding of the AIE and more importantly, for designing new AIEgens in particular in the context of induced assemblies, that for example to improve the fluorescence enhancement by preventing the efficient exciton-coupling.

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## Speciation analysis of manganese with the use of atomic spectrometry techniques

Anna Telk\*, Danuta Dudek-Adamska, Emilia Grygo-Szymanko, Stanisław Walas

Department of Analytical Chemistry, Jagiellonian University in Krakow, Krakow, Poland

\*anna.telk@uj.edu.pl

**ABSTRACT:** Sometimes, due to high detection limit of measurement techniques (e.g. electrochemical, nuclear magnetic resonance, NMR) or limited availability to required equipment (e.g. X-ray absorption near edge structure, XANES), the direct speciation analysis is inaccessible. In such cases hyphenated techniques allowing the separation of different species and selective determination at ultra-trace level are required. Here, popular separation techniques, like high pressure liquid chromatography (HPLC) and capillary electrophoresis (CE) are usually connected with atomic spectrometry techniques inductively coupled plasma mass spectrometry (ICP MS) and the analysis is preceded by sample fractionation with the use of extraction methods. In detailed speciation analysis, when species should be identified and determined by 2-dimensional analysis two different separation techniques (size exclusion chromatography and CE) and often two detectors: UV and ICP MS are required. Such complicated systems are used especially when biological samples (e.g. tissues or serum) are investigated. However, for water samples, when limited number of species is determined, sample matrix is simple, and analytes are in relatively high concentration, also simple methods can be proposed.

Herein, a simply and relatively cheap system for manganese speciation analysis is presented. The idea of this analysis was to determine both cationic and anionic forms of manganese together, after their separation on different sorbents by solid phase extraction, SPE. To improve the precision of the proposed method, a time-consuming and laborious separation step was realized in multicommutation flow system. What is more, a detailed evaluation of preconcentration conditions: a type and concentration of an eluent, pH of a sample, a loading time and method resistance to interference effects, was performed. Additionally, the results of manganese speciation in water samples obtained by the proposed method are compared with those obtained using ion pair chromatography high performance liquid chromatography coupled with ICP MS.

**Acknowledgment:** The research was partially financed by the National Science Centre, Poland, project no. 2013/11/D/ST4/02839.

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## Determination of Cadmium Content of Some Lipstick Samples by Direct Solid Sampling Atomic Absorption Spectrometry

Hande Tinas\*, Nil Ozbek, Suleyman Akman

Department of Chemistry, Istanbul Technical University, Maslak, Istanbul, Turkey.

\*tinash@itu.edu.tr

**ABSTRACT:** Lipstick is a very commonly used cosmetic product to change their natural colours of lips or just to moisturize them. There are 4 basic ingredients of lipsticks, wax, oil, alcohol and pigments. In order to add extra properties like glossiness and giving extra volume to lips, there are some other additions to ingredients. Mineral content of lipstick is mostly originated from colour pigments. Although metal content varied widely from brand to brand, it is found that women who apply lipstick two or three times daily can ingest a significant amount of aluminum, cadmium, chromium and manganese. Depending on the lipstick, in some cases women were meeting or surpassing the daily recommended exposure.

Cadmium is one of the most toxic elements in the world. It has no use to the body and is toxic even at low levels. The negative effects of cadmium on the body are numerous and can impact nearly all systems in the body, including cardiovascular, reproductive, the kidneys, eyes, and even the brain.

In this study, a practical method was proposed for the determination of Cd in different lipstick samples by solid sampling high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GFAAS). At first graphite furnace program is optimized for this highly complex matrix and 900°C for pyrolysis, 2300°C for atomization is selected with 3000°C/s heating ramp. In this study, it is proved that without very fast heating ramp, there is no atomization can be seen. Different modifiers were also tried and found no improvement. It is thought that since the sample is high oil content, modifiers do not penetrate inside the sample and show no effect. For calibration, Pd is used as a modifier to apply the same pyrolysis temperature as that of samples. After optimization of graphite furnace program, sample mass introduced to the furnace was optimized and the most appropriate sample amounts were 0.10-0.20 mg. In order to investigate homogeneity in the samples, each sample was analyzed 7 times and microscale heterogeneity of analyte distribution in samples were determined.

## Molecular and atomic emission spectroscopy of tyre rubber material from industrial production

Stefan Trautner<sup>\*A</sup>, Norbert Huber<sup>A</sup>, Wolfgang Spindelhofer<sup>B</sup>, Johannes Lackner<sup>B</sup>, Johannes Heitz<sup>A</sup>, Johannes D. Pedarnig<sup>\*A</sup>

<sup>A</sup>Institute of Applied Physics, Johannes Kepler University, Altenberger Straße 69, 4040 Linz, Austria;

<sup>B</sup>KRAIBURG Austria GmbH & Co. KG, Webersdorf 11, 5132 Geretsberg, Austria

\*stefan.trautner@jku.at

**ABSTRACT:** The molecular and atomic optical emission of laser-induced plasma on tyre rubber material is measured and the concentration of relevant analyte elements is quantified. The non-vulcanized rubber material is soft and it contains natural and synthetic caoutchouc and various other constituents (e.g., oil, soot) which makes LIBS analysis challenging. Sulphur and zinc oxide are added for vulcanization of the tyre material. The laser-induced breakdown spectroscopy (LIBS) measurements are performed in air using single pulses of a Nd:YAG laser ( $\lambda = 532$  nm, rep. rate 15 Hz) for excitation and a compact spectrometer with a CCD detector for time-resolved detection. For long integration times ( $\geq 20$   $\mu$ s) the LIBS spectra reveal intense molecular emission bands that mask the atomic emission lines of the analyte S in the near IR range. The NIR emission bands are due to CN molecules formed in the laser-induced plasma as confirmed by numerical simulations and by measurements in helium gas background [1]. However, measurements with helium gas flush or in vacuum [2] are not feasible in industrial production. For measurements in air we optimize the detector delay time and gate width which enables us to discriminate molecular and atomic emissions and to detect the S I emission lines around 920 nm with good signal/background ratio. The UV lines of Zn are not overlapped with other spectral features and can be easily measured in air. Calibration curves for Zn (213.9 nm) and for S (921.3 nm) are established. A rugged LIBS set-up for in-line measurements of tyre rubber in the industrial production is developed and the results of our tests will be presented.

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## Phase Correlation Applied to Image Processing in Laser-Induced Breakdown Spectroscopy

Jakub Vrábel<sup>A,\*</sup>, Jakub Klus<sup>A,B</sup>, David Prochazka<sup>A,B</sup>, Pavel Pořízka<sup>A,B</sup>, Jan Novotný<sup>A,B</sup>, Jozef Kaiser<sup>A,B</sup>

<sup>A</sup>CEITEC BUT, Central European Institute of Technology, Brno University of Technology, Purkyněova 123, 61200 Brno, Czech Republic; <sup>B</sup>AtomTrace, a.s., Kolejní 9, 61200 Brno, Czech Republic;

\*Jakub.Vrabel@vutbr.cz

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**ABSTRACT:** We extend the recent investigation of raw echellograms in Laser-Induced Breakdown Spectroscopy (LIBS) by utilization of phase correlation method, based on Fourier transform. Method, which is widely used in image registration, allows us to align echellograms with sub-pixel precision and enables estimation of changes in peak positions on detector image (i.e. echellogram).

Due to experimental conditions and instrumental setup, for example spectrometer temperature, position of peaks on echellogram (same as spectral lines) may vary. This behavior could be problematic in automatized approaches allocating each spectral line to database standard. Another issue is the influence of these fluctuations on experimental results and yielded statistics. Thus, image registration provides us means to mitigate or overcome these problems.

We indicate an improvement in analytical results of LIBS experiment, as limits of detection and relative standard deviation, after image registration. Another goal is measurement and theoretical description of main peak-shifting mechanisms on detector image.

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## High-resolution continuum source graphite furnace molecular absorption spectrometry as an alternative to GC-MS for the direct determination of chlorinated persistent organic pollutants in fish oil

Bernhard Welz<sup>\*A,B</sup>, Éderson R. Pereira<sup>A</sup>, Josias Merib<sup>A</sup>, Heloisa R. Cadorim<sup>A</sup>, Mauana Schneider<sup>A</sup>, Gabriel S. Carvalho<sup>C</sup>, Fabio A. Duarte<sup>C</sup>, Javier del Campo Menoyo<sup>D</sup>, Joerg Feldmann<sup>E</sup>

<sup>A</sup>Departamento de Química, Universidade Federal de Santa Catarina, Campus Trindade, 88040-900 Florianópolis - SC, Brazil; <sup>B</sup>Instituto Nacional de Ciência e Tecnologia do CNPq – INCT de Energia e Ambiente, Universidade Federal da Bahia, Campus Ondina, Salvador – BA, Brazil; <sup>C</sup>Departamento de Química, Universidade Federal de Santa Maria, 97105-900 Santa Maria - RS, Brazil; <sup>D</sup>Golden Omega S.A., Av. Comandante San Martín 3460, Lote B-2, Arica, Chile; <sup>E</sup>Trace Element Speciation Laboratory (TESLA), Department of Chemistry, University of Aberdeen, Scotland, UK

\* w.bernardo@terra.com.br

**ABSTRACT:** In the aquatic environment, persistent organic pollutants (POPs), mainly organochlorine pesticides and polychlorinated biphenyls, can accumulate in fish lipid tissues due to their high hydrophobicity, and become this way one of the main sources of human exposure to POPs through the consumption of fish meat and oil as Omega-3 source. The occurrence of (POPs), was directly associated with several diseases and environmental endocrine disrupting. Chlorine might serve as a proxy for the presence of POPs, and a fast screening of chlorine in a complex matrix, such as fish oil, could provide substantial information about the contamination with POPs. Therefore, a method has been developed in this work for the determination of total chlorine in fish oil samples via molecular absorption of the strontium mono-chloride molecule in the gas phase using high-resolution continuum source graphite furnace molecular absorption spectrometry. The effect of zirconium as permanent chemical modifier in the pyrolysis and vaporization stages was optimized in order to avoid the need for any kind of sample preparation prior to the determination of total chlorine, using just a dilution with 1-propanol. The accuracy has been evaluated using micro-coulometric titration after sample combustion, and the values were statistically in agreement (95% confidence level) between both techniques. The method has been applied for the determination of total chlorine in five different fractions of a commercial pooled marine fish oil sample collected from the Pacific Ocean, where the majority of the fish is Peruvian anchovy (*Engraulis ringens*), two commercial oils from Brazil and three Omega-3 supplements acquired in Germany. The limit of detection of the procedure is 1.8 ng Cl absolute or 0.9 µg g<sup>-1</sup> Cl in the fish oil. The time required for a single determination is less than 5 min, and less than 15 min for a triplicate determination.

## New vapor generation methods based on plasma chemical/electrochemical processes

Zhenli Zhu\*, Xing Liu, Dong He, Hongtao Zheng

State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan, China.

\*zlzhu@cug.edu.cn

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**ABSTRACT:** In this study, new high efficiency vapor generation strategy was proposed based on plasma chemical/electrochemical processes for the elemental by atomic fluorescence spectrometry. In plasma electrochemical approach, a solution anode glow discharge glow discharge microplasma was acted as a gaseous cathode to initiate the plasma electrochemical vapor generation of Cd and Zn. Cadmium/Zinc ions could be converted into molecular species efficiently at the plasma-liquid interface from a supporting electrolyte (HCl, pH=3.2). It was found that the overall efficiency of the plasma electrochemical vapor generation (PEVG) system was much higher than the conventional electrochemical hydride generation (EchG) and HCl-KBH<sub>4</sub> system. With no requirement for other reducing reagents, this new approach enabled us to detect Cd and Zn with detection limits as low as 0.003 µg/L for Cd and 0.3 µg/L for Zn. Good repeatability (relative standard deviation (RSD), n = 5) was 2.4% for Cd (0.1 µg/L) and 1.7% for Zn (10 µg/L) standard. The accuracy of the proposed method was successfully validated through analysis of cadmium in reference material of stream sediment (GBW07311), soil (GBW07401), rice (GBW10045), and zinc in simulated water sample (GSB 07-1184-2000). Replacing a metal electrode with a plasma offers the advantage of eliminating potential interactions between the species in liquid and the electrode, which solves the issues associated with electrode encountered in conventional EchG. The ability to initiate electrochemical vapor generation reactions at the plasma-liquid interface opens a new approach for chemical vapor generation based on interactions between plasma gas-phase electrons and solutions. In plasma chemical approach, a novel vapor generation method for lead was developed based on dielectric barrier discharge induced plasma. Under the optimized conditions, the detection limit of Pb was found to be 0.003 µg/L; good repeatability (relative standard deviation (RSD) = 1.7%, n = 5) was obtained for a 1 µg/L Pb<sup>2+</sup> standard. The accuracy of the proposed method is demonstrated by successful analysis of Pb in reference material of stream sediment (GBW07311), soil (GBW07403), basalt (BCR-2), and simulated water sample (GBW08601). These study clearly demonstrated that plasma induced chemical/electrochemical processes provides a novel green vapor generation approach for elemental determination

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## LIBS Analysis of aluminum alloys: An Alternative Approach

Milos Momcilovic, Sanja Zivkovic\*, Milan Trtica, Jelena Savovic,

Institute of Nuclear Sciences Vinca, University of Belgrade, Serbia.

\*sanjaz@vinca.rs

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*ABSTRACT: Analytical potential of unique laser-induced breakdown spectroscopy (LIBS) system for qualitative and quantitative analysis of aluminum alloy samples in air at atmospheric pressure was demonstrated. The proposed cost effective non-gated LIBS system uses pulsed nanosecond Transversely Excited Atmospheric Carbon dioxide (TEA CO<sub>2</sub>) laser as the laser light source in conjunction with time-integrated space-resolved (TISR) emission spectroscopy for the acquisition of emission spectra. To our best knowledge, the possible use of infrared TEA CO<sub>2</sub> laser induced plasma for elemental characterization of aluminum alloys was not examined before. Linear calibration curves for Mg, Cr, Cu and Fe were obtained using aluminum spectrochemical standards. The limits of detection were in the 2-73 ppm range depending of elements. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used as a reference technique to estimate the accuracy of LIBS determination by use of control samples with known compositions. The advantages of the proposed LIBS system are simplification of the instrumentation and improved limits of detection compared to standard LIBS with Nd:YAG laser and time-gated detection.*

### Reference

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## Do 1-aminopyrene, 1-hydroxymetilpyrene, carbendazim and carbaryl interact with biosubstrates and micelles?

Tarita Biver, Stefania Giannarelli\*, Francesca Macii

Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via G. Moruzzi 13 – 56124 – Pisa, Italy.

\*stefania.giannarelli@unipi.it

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**ABSTRACT:** Organic pollutants as polycyclic aromatic hydrocarbons (PAHs) and pesticides are nowadays ubiquitous (*Eco-toxicology*, 22, 2013, 240-250). PAHs and pesticides are highly lipophilic and all at least suspected of carcinogenic effects (*Journal of Enviromental Science and Health*, 20, 2002, 149-183; *Journal of Toxicology and Environmental Health Part B*, 15, 2012, 238-2632). Information on their toxic activity is often related to in vivo studies, whereas a detailed analysis of the mechanistic/chemical aspects of the binding to biosubstrates is sometimes missing.

To contribute to this field and in the frame of our participation to PNRA (National Antarctic Research Program) we have carried out some tests on the binding of two PAHs (1-aminopyrene and 1-hydroxymetilpyrene) and two pesticides (carbendazim and carbaryl) to biosubstrates as natural DNA and the protein bovine serum albumin (BSA). The interaction with micelles and liposomes was also tested, both as to scale the lipophilicity of these species and to get information of the possible accumulation on membranes. The results collected show that the high hydrophobicity of these species turns into very high affinity for DNA. Absorbance and fluorescence titrations suggest complex binding modes that are discussed in relation with the different pollutant/DNA ratio. BSA binding is also found to occur in the case of the two PAHs.

Ultrafiltration coupled with absorbance spectroscopy enables the percentage of retention (R%) on the micelle/liposome be measured. R% dependence on the molecule and on the type of system (sodium dodecyl sulphate anionic micelles, TritonX-100 neutral micelles, dodecyl trimethyl ammonium chloride positive micelles and 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine liposomes) is discussed.

---



## Detecting products from the electrooxidation of renewable alcohols with SNIFTIRS technique

Marco Bellini, Maria G. Folliero, Jonathan Filippi, Maria V. Pagliaro, Andrea Marchionni\*,  
Hamish A. Miller, Francesco Vizza

Istituto di Chimica dei Composti OrganoMetallici, Consiglio Nazionale delle Ricerche,  
via Madonna del Piano 10 – 50019 Sesto Fiorentino (FI), Italy

\*andrea.marchionni@iccom.cnr.it

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*ABSTRACT: The Subtractively Normalized Interfacial Fourier Transform Infrared Spectra (SNIFTIRS) technique is commonly used in electrochemistry to study adsorbed species on the surface of the working electrode or intermediate species formed in the thin electrolyte layer. We used SNIFTIRS to study the formation of organic molecules from the electrooxidation of renewable alcohols (ethanol, ethylene glycol and glycerol) in alkaline media on different electrocatalysts. The results showed a high pH dependence of the selectivity of each electrocatalyst, in particular it was seen that Pd based catalysts become active towards C-C bond cleavage at pHs lower than 12. On the basis of these results, we also propose the reaction mechanism for alkaline alcohol electrooxidation.*

---

## Uptake of Nanoparticles by Fresh Water Algae using Single Cell ICP-MS

Chady Stephan<sup>\*A</sup>

<sup>A</sup>PerkinElmer Canada, 501 Rowntree Dairy Road, Woodbridge, Ontario, Canada;

\*chady.stephan@perkinelmer.com

---

*ABSTRACT: The exposure and dose of nanoparticle (NP) contaminants to cells in either human or environmental health is a subject of great interest and debate. In the medical profession it is important to know how much of a NP containing drug is actually entering the target cells, and in the environment it is important to know whether NPs from consumer products are affecting the eco system but interacting with algae or bacteria and if these can then be trophically transferred through the food chain. It is generally accepted that desirable metrics for measuring exposure and dose in this case would be particles per mL (part. / mL) and concentration per cell (conc. / cell) respectively. However because of instrument limitations these have both been measured using ionic mass concentration which means there is some vital missing information.*

*Here we exposed various strains of freshwater algae to Au NPs and Au ions. We show that single cell ICP-MS (SC-ICP-MS) was able to measure the number of NPs in the suspension media (exposure), the number of cells containing metal (% uptake) and finally the amount of metal within those cells (dose) in various different species of fresh water algae cell. We show that although the exposures are kept constant (ionic concentration of 1 ppb, equating to a NP concentration of around 500,000 part. / mL the dose and response is highly dependent on the algae strain.*

---

## Sonically prepared Cu-MFI and Cu-USY zeolites as catalysts for DeNO<sub>x</sub> processes.

Ł. Kuterasiński<sup>A</sup>, P. Jodłowski<sup>A\*</sup>, A. Dziejnicka<sup>A</sup>, R. Jędrzejczyk<sup>B</sup>, D. Chlebda<sup>C</sup>

<sup>A</sup>Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Kraków, Poland, <sup>B</sup>Malopolska Centre of Biotechnology, Gronostajowa 7a, 30-387 Kraków, <sup>C</sup>Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Cracow, Poland

\*jodlowski@chemia.pk.edu.pl

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**ABSTRACT:** One of the problems associated directly with environmental protection is the presence of harmful pollutants in air. Nitrogen oxides (NO<sub>x</sub>) have a negative influence on health and human life, and due to the solar radiation react and form the so-called photochemical smog. Nitrogen oxides may be present in effluent gases from various sources: automotive, energetics and heavy industry. One of the possible abatement of nitrogen oxides is the selective catalytic reduction (SCR DeNO<sub>x</sub>). The aim of this paper was to study Cu-MFI and Cu-USY type zeolite as catalysts for selective catalytic reduction of NO<sub>x</sub>. Sonochemical preparation of Cu species on the surface of zeolites may be used for the preparation of catalysts used for environmental purposes. Ultrasonic irradiation of aqueous copper nitrate solution causes acoustic cavitation. That leads to bubble collapse and formation of intense and short-term local heating and high pressures, which facilitate incorporation of Cu species into zeolite structure. MFI and USY zeolites were sonicated in situ at 20°C for 20 min in an 0,5 M aqueous solution of Cu(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O. Additionally, classical ion-exchanged zeolites were also prepared. Prepared catalyst samples were examined by various characterisation methods such as: XRD, BET and AAS method. Sorption and acidic properties of the prepared catalysts were determined by in situ IR methods using NH<sub>3</sub>, CO and NO as a probe molecules. The catalytic activity of prepared Cu-MFI and Cu-USY was measured in Hidden Analytical Catlab plug-flow reactor equipped with quadrupole mass spectrometer. XRD analysis confirmed pure MFI and USY type phase of the studied samples. Acidity measurements (NH<sub>3</sub>-IR, CO-IR) carried out for all studied samples indicated the presence of Brønsted and Lewis acid sites. In case of USY catalysts, higher concentration of the latter type of acid centres was found, which may be explained by higher Cu content in this type of zeolite in comparison with MFI. The type of modification of MFI and USY zeolite has small influence on acidity. Sonicated zeolites exhibited somewhat higher concentrations of both types of acid sites.

---

The Project was financed by the National Science Centre Poland based on the decision No 2015/17/D/ST8/01252 and partly within National Centre for Research and Development No LIDER/204/L-6/14/NCBR/2015.

## Influence of the Spot Size on ZnO Thin Films Produced by Pulsed Laser Deposition

A. Yáñez-Guzmán<sup>A</sup>, A. Fernández<sup>A</sup>, C. Sánchez Aké<sup>\*A</sup>, T. García-Fernández<sup>B</sup>, M. Villagrán-Muniz<sup>A</sup>

<sup>A</sup>Laboratorio de Fotofísica, Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México, Apartado Postal 70-186, Cd. Mx., C.P. 04510, México; <sup>B</sup>Universidad Autónoma de la Ciudad de México (UACM), Prolongación San Isidro 151, San Lorenzo Tezonco, Cd.Mx, C.P. 09790, México.

\*citlali.sanchez@ccadet.unam.mx

**ABSTRACT:** It is well known that the characteristics of thin films produced by pulsed laser deposition (PLD) depends on the properties of the ablation plume since it provides the material flux for film growth<sup>[1]</sup>. For this reason, there are several works of PLD that study the effect of the deposition conditions on the thin films. However, an important number of papers report only the laser fluence employed for deposition without specifying the laser beam spot size and beam energy. In particular, the laser beam spot size affects the dynamics of the plume expansion<sup>[2]</sup> and the ablation rate<sup>[3]</sup>, therefore this parameter can change the characteristics of the deposited film. To investigate this effect, we deposited ZnO thin films by laser ablation and employed time-resolved optical emission spectroscopy to study the expansion of the plasma plume produced with various spot sizes. All experiments were performed in the presence of O<sub>2</sub> gas, using ns laser pulses at a fixed fluence of 2 J/cm<sup>2</sup>. The temporal evolution of the electron density and temperature was determined as a function of the distance along the normal direction to the target surface. The composition, crystalline structure and optical properties of the films were compared with the plasma parameters. Our results demonstrate that the composition of the films, the thickness of the films and their transparency strongly depend on the spot size of the laser beam even for a fixed laser fluence.

[1] D.B. Chrisey and G.K. Hubbler (1994). Pulsed laser deposition of thin films. United States, John Wiley and Sons.

[2] S.S. Harilal, Influence of the spot size on propagation dynamics of laser-produced tin plasma, J. Appl. Phys. 102, 123306, 2007.

[3] M.E Shaheen, J.E. Gagnon, B.J. Fryer, Excimer laser ablation of aluminum: influence of spot size on ablation rate, Laser Phys. 26, 116102, 2016.

## *Wine tasting*



**Wine tasting venue:** CongressCenter, the conference building

**Wine tasting date:** Monday, June 12<sup>th</sup>

**Wine tasting time:** 18.30 (after Poster session I)

We organized, together with Fattoria di Petroio ([www.fattoriapetroio.com](http://www.fattoriapetroio.com)) a wine tasting event for all conference participants.

Nested in the heart of Tuscany's beautiful Chianti hills, just a few miles North of Siena, lies the Fattoria di Petroio, which produces wine (especially Chianti Classico) since 1924. Today, the 9 hectares of vineyards, enable Petroio to produce, with great passion and dedication, a yearly average of 25000 bottles of traditional and territorial Chianti Classico; 5000 bottles of the harvest's best juice, the Chianti Classico Riserva, 5000 bottles of fresh, readily drinkable IGT Rosso Toscano called Poggio al Mandorlo, and the Barbera Pomorosso.

During this experience, you will have the occasion to taste three local wines, together with olive oil produced by Fattoria di Petroio and a selection of cheese from a producer from Maremma.

The wine tasting experience is kindly sponsored by XGLab.





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## *Concert Information*

**Concert venue:** Cathedral Square, Piazza dei Miracoli (Square of Miracles), Pisa

**Concert date:** Tuesday, June 13<sup>th</sup>

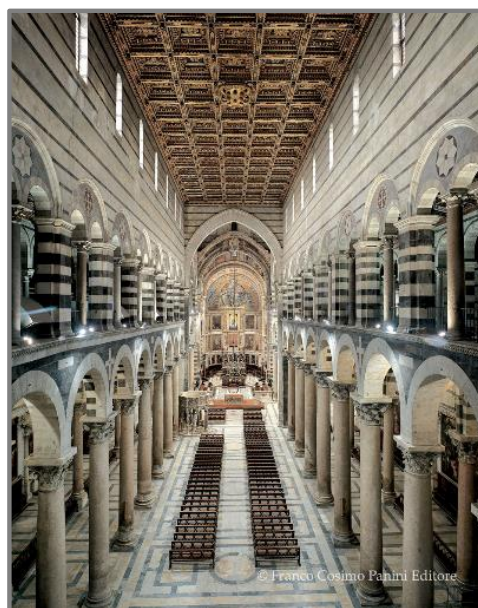
**Concert time:** 21.00 (doors will close at 20.30)

**How to arrive:** take LAM Rossa at the train station (every 10 min; direction Pietrasantina Parking; bus stop: Piazza Manin).

**Entry points:** Cathedral facade and Bonanno Gate, in front of the Tower.

Enjoy a memorable experience at the medieval Cathedral of Pisa. Riccardo Donati, the chapel master of the Cathedral of Pisa, will perform an organ concert specially for us. The proposed repertoire includes Johann Sebastian Bach, Felix Mendelssohn, Louis Vierne and Cesar Franck.

**For security reasons, in order to be able to attend the concert, participants must bring the entrance ticket with them. Access to the Cathedral would not be granted without the entrance ticket.**





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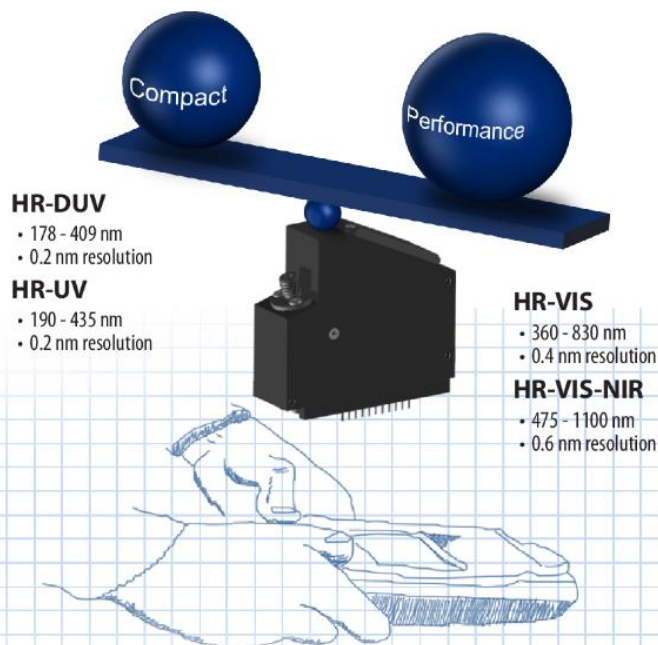
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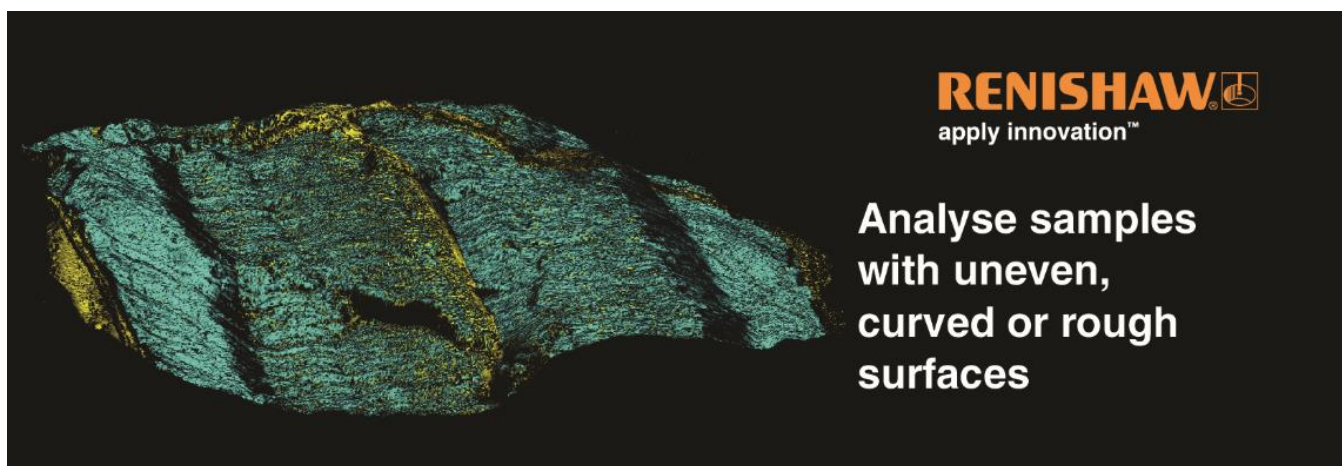
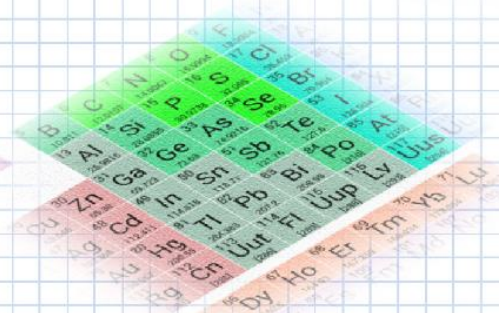
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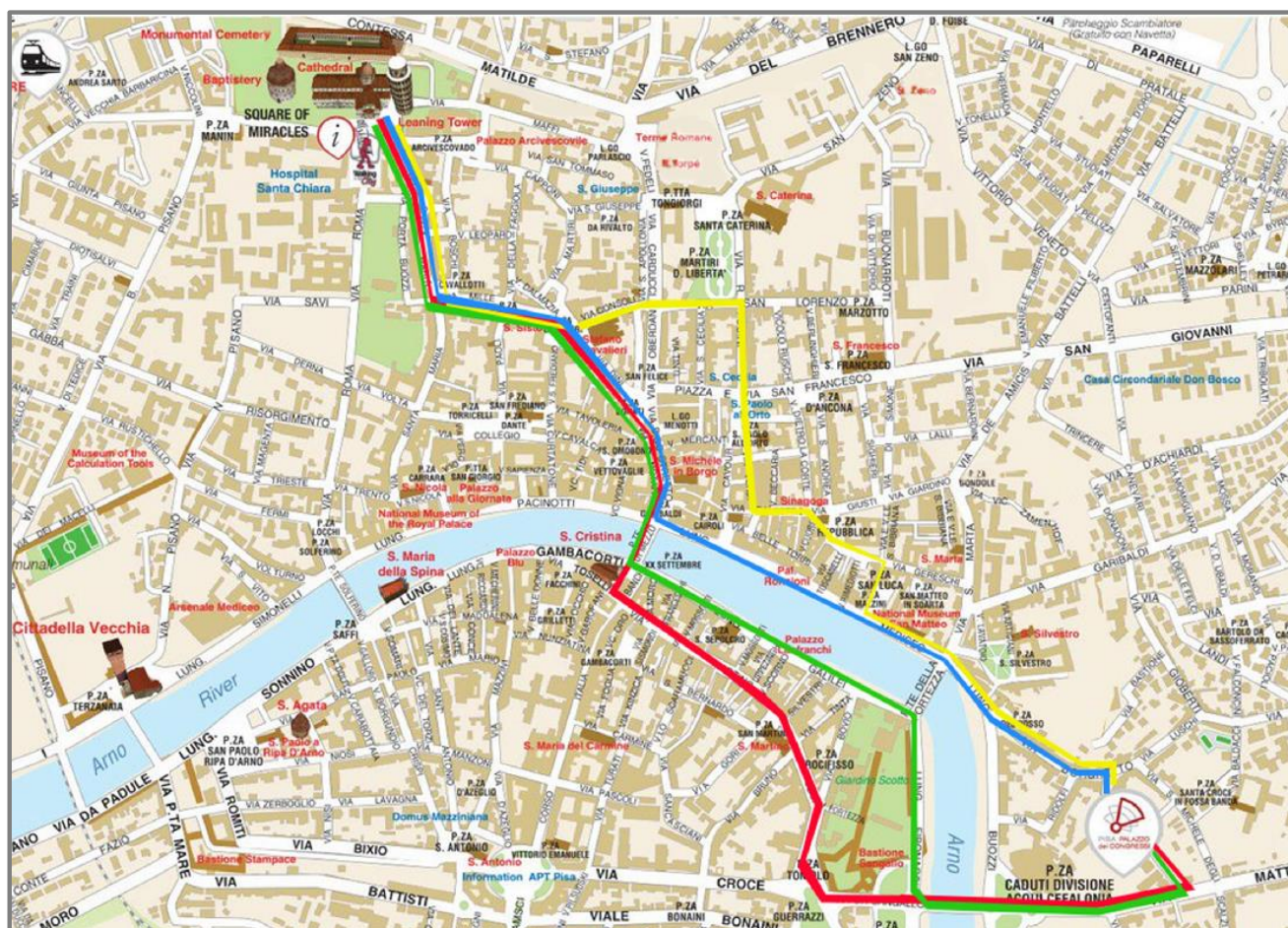


## Excursion information

**Excursion date:** Wednesday, June 14<sup>th</sup>

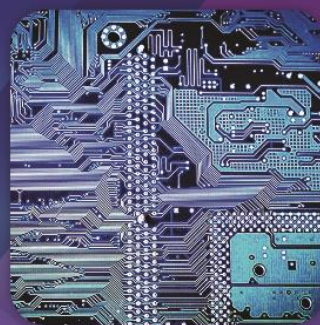
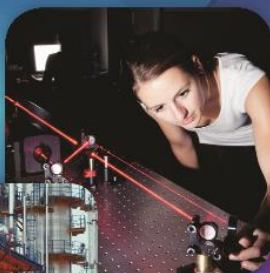
**Excursion duration:** about 2 hours

**Excursion itinerary:** The participants will be accompanied by professional guides to the discovery of the hidden treasures of the Old City of Pisa. The tour will start from the Congress Center; four different itineraries are proposed (see the attached figure). You are kindly asked to choose one of them at the Conference desk, where you will be given a ticket of the corresponding color (see map) and an earpiece for listening to the guide explanations (in English). To avoid congestions in the narrow alleys of the Old City, the groups will leave with a delay of 10 minutes from the previous one. Please check your ticket for the exact departure time. All the itineraries will converge to Piazza dei Miracoli, where a tour of the Cathedral and Monumental Cemetery is scheduled.





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## *Gala Dinner information*

**Venue:** Stazione Leopolda, Piazza Federico Domenico Guerrazzi, 11, Pisa

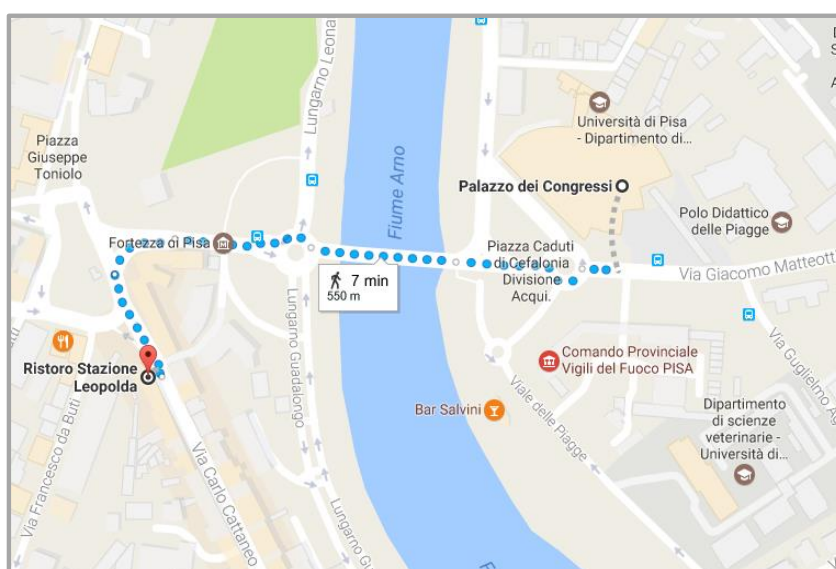
**Gala dinner date:** Wednesday, June 14<sup>th</sup>

**Gala dinner time:** 20.00

**Distance by foot:** 7 min from the Congress Center ([see map](#)).

Social dinner is included in the registration fee for participants and accompanying persons. Extra tickets will be available at the Conference desk (€ 70 each).

**For security reasons, in order to be able to attend the gala dinner, participants must bring the corresponding ticket with them.**





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